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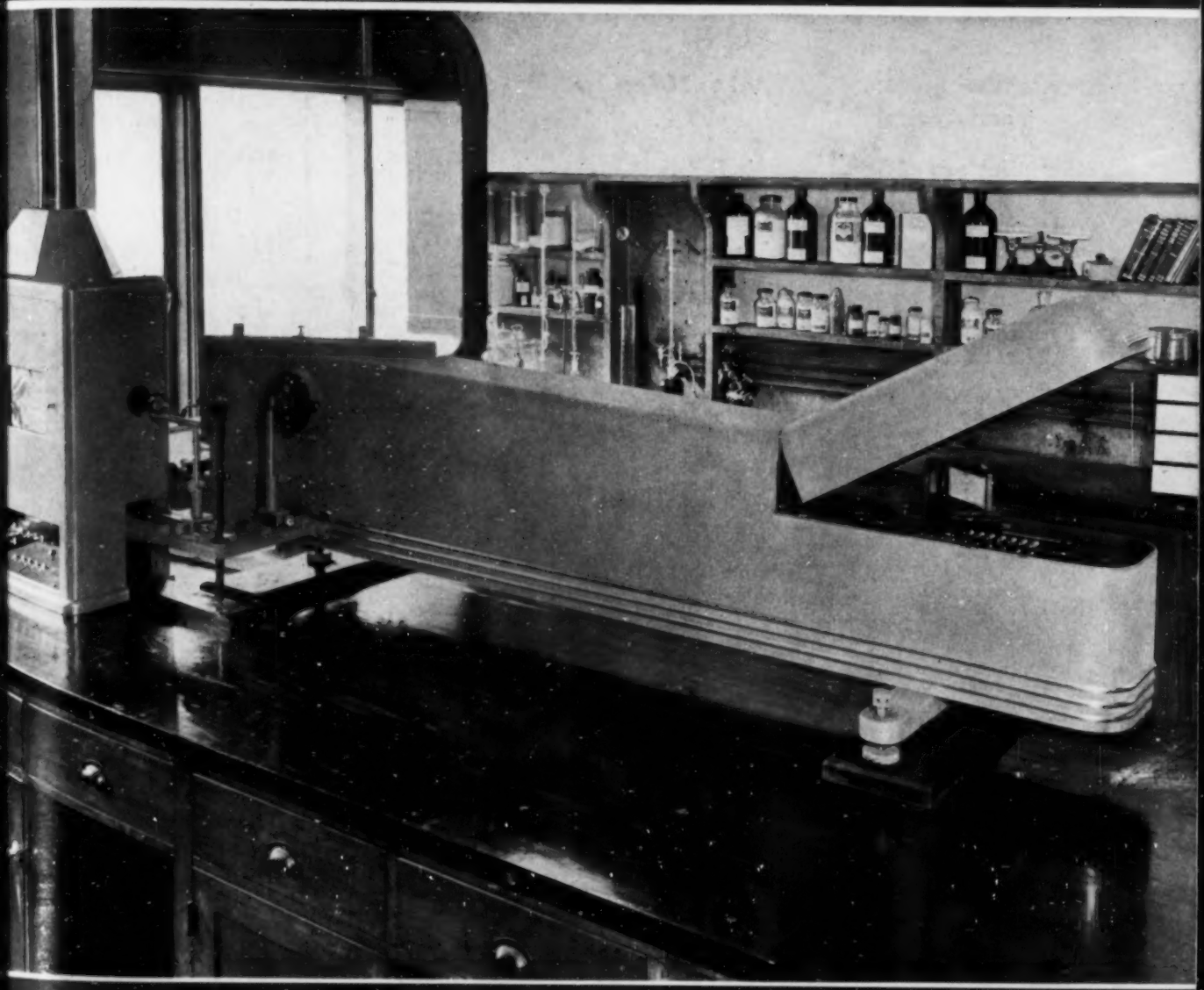

Modern spectrographic installation

JOURNAL OF APPLIED
PHYSICS

NOVEMBER, 1939 Vol. 10, No. 11

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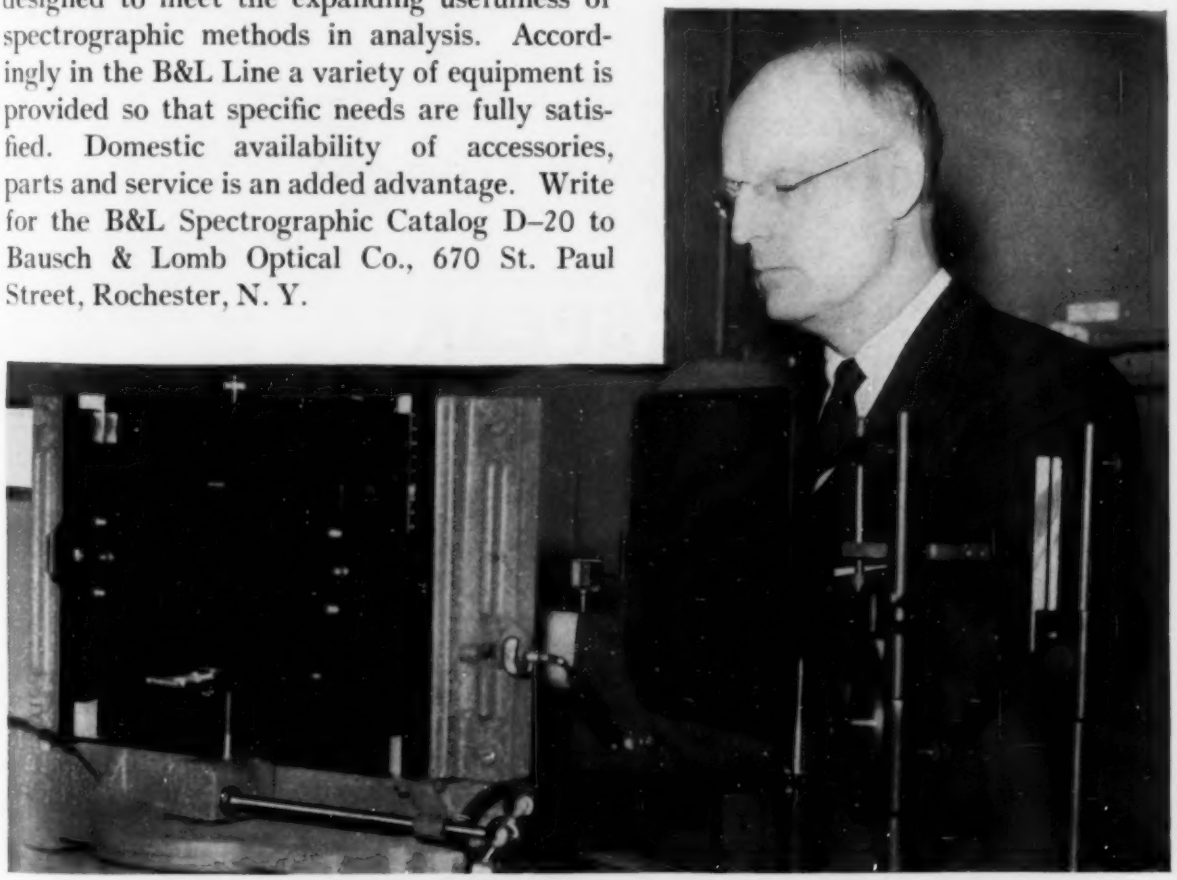

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Research and Preparedness

ONCE more a major war has been thrust upon mankind. It is generally conceded at the present time that the most effective method of staying out of a war is that of being prepared. Most people think of battleships, cannons and airplanes when they speak of preparedness. While these are certainly necessary there is another and perhaps a more subtle form of preparedness which we wish to emphasize here. We have in mind active research of a military character. Let us summarize the principal auspices under which research preparedness is being carried out.

First of all we have the National Research Council which was set up in 1916 to assist in preparedness at that time. The National Research Council has been doing a splendid service in the encouragement of fundamental research. Undoubtedly it is ready again to organize the present research resources of the country on a wartime basis if the need arises. The Navy has the Naval Research Laboratory, a description of which appeared recently in this Journal. The National Advisory Committee for Aeronautics sponsors fundamental aeronautical research. The Langley Memorial Aeronautical Laboratory is said to be one of the largest and best equipped aeronautical laboratories in the world. Research of a military character is also being carried out by the National Bureau of Standards, the Bureau of Mines and by other governmental agencies.

Rather conspicuously absent from the above list is research sponsored by the War Department itself. Without doubt some of the research agencies referred to are supported in part by War Department funds, but it seems strange that there is no large research laboratory under the immediate direction of the War Department. One would expect a laboratory devoted to the application of physics, chemistry, metallurgy and engineering to the production of war materials. Such a laboratory would naturally carry on applied research of a military character but it could also develop certain lines of fundamental research in university laboratories as well as in its own laboratories. Such fundamental subjects as ballistics are receiving scant attention at the present time.

It is not the intention of this note to stress the lack of research preparation in any one branch of the government. We are interested primarily in seeing a larger proportion of the huge funds spent for preparedness used for preparedness in research. Unless we go to war, *every cent* that is spent on battleships, armament, etc., gradually vanishes in depreciation and obsolescence. On the other hand, money spent on research repays over and over the initial expenditure in peace times as well as in war times.

Spectroscopy

This issue of the Journal of Applied Physics is devoted to recent advancements in the field of applied spectroscopy. The papers are concerned with spectroscopic apparatus, atomic and molecular emission spectra, absorption spectra, spectroscopy of the infra-red, compilations of data and applications of spectroscopy in astrophysics. One paper on x-ray spectra scheduled for this issue is to be held for the December issue. For this fine group of papers we are especially indebted to Dr. William F. Meggers, our associate editor. He suggested the subjects and the authors, and has given much advice in the preparation of the issue.

Spectroscopic Apparatus

BY WILLIAM F. MEGGERS

Spectroscopy Section, National Bureau of Standards, Washington, D. C.

THE past 25 years have witnessed unprecedented advances in the interpretation of atomic and molecular spectra by means of the quantum theory, and in the practical use of spectra for quantitative chemical analysis. These developments in pure and applied spectroscopy have entailed many improvements in spectroscopic apparatus, a review of which is the purpose of this article. No attempt will be made to distinguish the apparatus used in pure research from that employed in practical applications because in general it is the same, and often the scientific device of one era becomes the technical tool of the next as illustrated by the Geissler tube of yesterday and the luminous gas advertising or lighting of today.

Spectroscopic apparatus may be classified under (1) spectroscopes and spectrographs, (2) interferometers, (3) comparators, (4) microphotometers, and (5) light sources.

1. Spectroscopes and Spectrographs

The glass prism is undoubtedly the oldest man-made apparatus for separating composite light into its components; the first scientific experiments with it appear to be those reported by Sir Isaac Newton in 1672. A complete spectroscope, consisting of slit, collimator lens, prism and telescope, was first assembled about a century ago, and the form given to it by Kirchhoff and Bunsen (Fig. 1) in 1860 remains essentially the same today. At the present time the most commonly used visual spectroscope is probably the constant deviation wave-length type (Fig. 2) introduced by Adam Hilger, Ltd., in 1904. Provided with calibrated wave-length scales coiled on a drum connected with the rotating prism, the best of these instruments enable one to measure with an average accuracy of 1 or 2A from 3900 to 8000A. However, visual observations have gradually given way to photographic recording because of enormous advantages possessed by the latter method. Photography extends the observations to invisible spectral regions, integrates the energy from light sources and gives a complete and permanent record. In principle, the spectroscope becomes a spectrograph when a photographic plate or film is substituted for the eyepiece. But another substitution is required if the ultraviolet is to be observed; glass which is opaque to short waves must be replaced by transparent crystal optics. For prism spectrographs, the material most commonly used is natural quartz, but because of birefringence in these crystals, it is necessary to use equal amounts of left- and right-handed quartz to avoid double images of the slit. Thus, a 60° prism is made (after Cornu) of two 30° prisms, so that the rotation occurring in one is exactly compensated by the reverse rotation in the other (Fig. 3). Prism spectrographs employing the principle of autocollimation accomplish this by use of a Littrow quartz prism with a rear reflecting surface (Fig. 4) that reverses the path of light through prism and lens, thus compensating rotation of polarization in one direction by an equal rotation in the opposite direction.

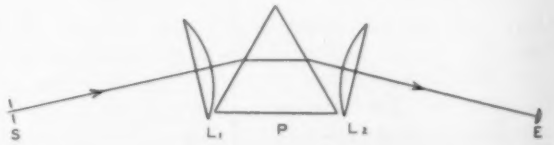

FIG. 1. Bunsen spectroscope, S = slit, L_1 = collimator lens, $P = 60°$ prism, L_2 = telescope lens, E = eyepiece.

For a given power, the latter type of spectrograph requires less quartz (or glass), but is open to the objection that scattered light (from lens reflections) is unavoidable. This background is minimized by tilting or masking the lens and sacrificing the best definition.

Both types of quartz spectrographs are widely

used for spectrochemical analysis and both are commercially supplied with interchangeable quartz and glass optics. To increase the resolving power of either, it is necessary to employ larger or multiple prisms at greatly increased expense. The trend has been to standardize on a few sizes of Cornu and Littrow prisms. At the moment the most popular model of Cornu prism spectrograph is one with lenses of 50 to 60 cm focal length and about 5 cm aperture, recording the spectrum from 2000 to 8000A on a 25-cm (10-inch) plate. The largest and most powerful prism spectrographs are generally of the autocollimating type, and a majority of the Littrow prism instruments now used for testing have a lens of about 7 cm diameter and focal length of about 175 cm (for yellow light). These give a spectrum about 70 cm long from 2000 to 8000A which can be recorded on 3 or more plates, each 25 cm long. The adjustments of the spectrograph for each plate

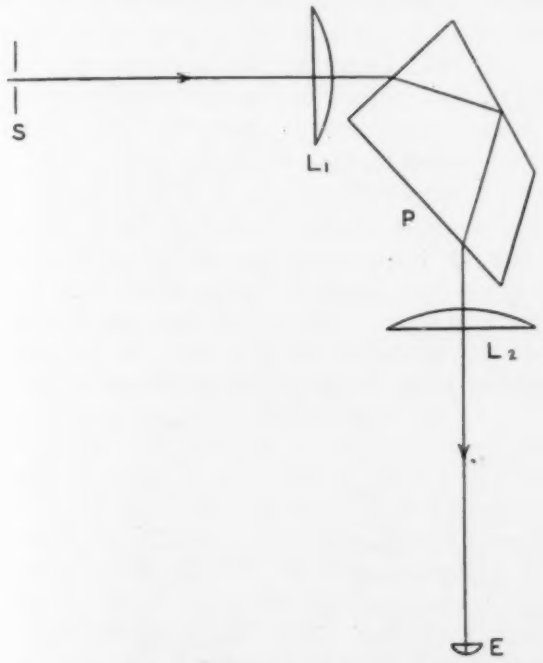

FIG. 2. Constant deviation spectroscope, S = slit, L_1 = collimator lens, P = Pellin-Broca prism, L_2 = telescope lens, E = eyepiece. Wave-length measuring drum not shown.

consist of prism rotation, camera focus and inclination of plate, but one instrument maker has recently succeeded in making these three adjustments automatically and simultaneously by one control. Furthermore, glass optics, giving

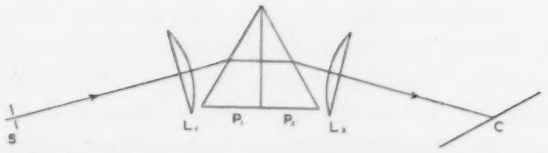

FIG. 3. Cornu quartz spectrograph. S = slit, L_1 = collimator lens of left-handed quartz, P_1 = 30° prism of left-handed quartz, P_2 = 30° prism of right-handed quartz, L_2 = camera lens of right-handed quartz, C = camera.

FIG. 4. Littrow quartz spectrograph. S = slit, P_1 = totally-reflecting quartz prism, L = autocollimating quartz lens, P_2 = Littrow quartz prism, C = camera.

better performance in the visible spectrum, may be substituted for quartz optics without damage to the reproducibility of adjustments for either glass or quartz.

Historically the second—but in truth the most important—instrument for the analysis of light is the diffraction grating, first made, studied and used by Fraunhofer in 1822. The ruled diffraction gratings now available surpass prism spectrographs in dispersing and resolving powers. Furthermore, these powers remain practically constant throughout a grating spectrum, whereas in prisms they are functions of the wave-length. Concave diffraction gratings are self-focusing spectrographs whose freedom from all absorbing material make them uniquely useful in the spectral extremes. Thus they serve to study 10 octaves of ultraviolet including Röntgen rays, and many octaves of infra-red. In fact, Rowland's invention of the concave grating in 1882 has benefited spectroscopic research more than any other device with the possible exception of the photographic plate.

Although giving outstanding service to research, diffraction gratings have been slow to find favor among practical spectrographers. Some of the reasons are low average light efficiency, under supply, and fear of ghosts, but these objections have all but vanished since the recent introduction of improvements in ruling machines and metalized surfaces leading to the production of brighter spectra and practical elimination of spurious images.[1] The relative merits of prism and grating spectrographs for spectrochemical

testing have lately been discussed in detail,[2] and one paper from the same point of view has compared various ways of mounting concave gratings.[3] At the present time, three or more types of concave grating spectrographs are manufactured and sold. They may be described as the Rowland or Abney,[4] Wadsworth,[5] and Eagle[6] mountings in honor of their inventors, and are shown schematically in Figs. 5, 6, 7 on the same scale. Gratings ruled with 15,000, 24,000, or 30,000 lines per inch are gradually increasing in popularity for industrial testing and for astrophysical research. The future seems to be brighter for ruled gratings than for quartz prisms, but the choice of a spectrograph either for a specific purpose or for general applications will always depend on so many factors that no final decision should be made without weighing all the facts.

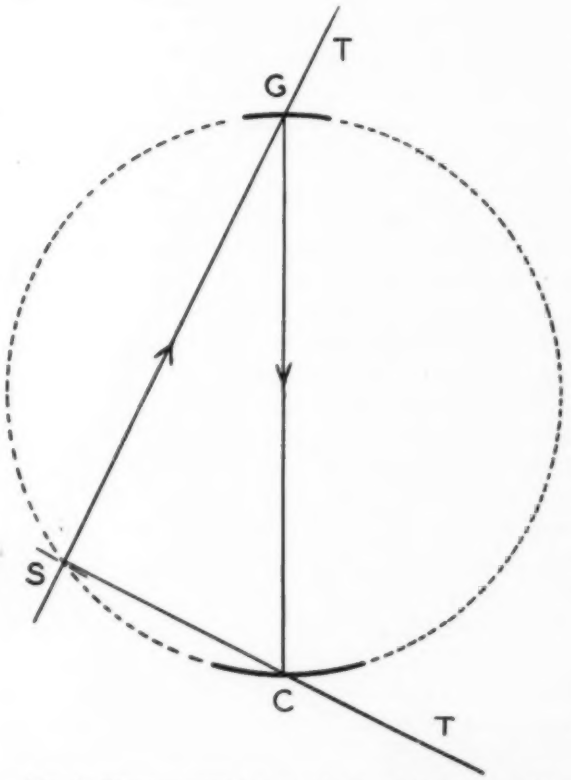

FIG. 5. Concave grating, Rowland or Abney mounting. S=slit, G=diffraction grating, C=camera, T=track. Rowland mounting S fixed, G and C moveable, Abney mounting vice versa.

2. *Interferometers*

Interferometer is a generic term for interference spectroscope especially designed to obtain high resolving power or precision in measurement. Four different types of interferometers are described in all textbooks of physical optics or advanced physics; they are the so-called Michelson interferometer, the echelon (also invented by Michelson), the Fabry-Perot, and the Lummer-Gehrcke, schematically shown in Figs. 8, 9, 10, 11. To separate the interference patterns of 2 or more radiations observed simultaneously, it is necessary to cross an interferometer with a stigmatic spectroscope or spectrograph.

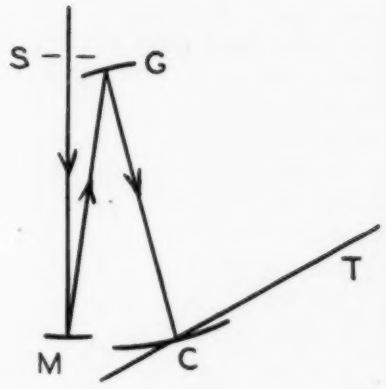

FIG. 6. Concave grating, Wadsworth stigmatic mounting. S=slit, M=mirror, G=grating, C=camera, T=track.

It is noteworthy that no new instruments of this class have been devised since the beginning of the present century, but various applications of the familiar types have suggested modifications of some of them. First of all, it must be admitted that the Michelson echelon, and the Lummer-Gehrcke interferometers have declined in popularity to the point where they are now rarely mentioned in research, whereas the Michelson and Fabry-Perot types have found increasing usefulness in both research and testing. Thus, it is common knowledge (at least among physicists) that independent and remarkably accordant measurements of the meter in terms of light waves have been made with the Michelson interferometer and with the Fabry-Perot interferometer. Also, it is well known that the latter instrument has given us international secondary standards of wave-length in a considerable range of spectrum and that these standards are important for spectroscopy, astrophysics and metrology. As examples of the application of interferometer principles to practical metrology, the absolute measurement of "end gages"

(Johansson blocks) by employing the principles either of the Michelson interferometer[7] or of the Fabry-Perot interferometer[8] may be mentioned. The use of the Fabry-Perot interferometer for measurements of refractivity and dispersion may be illustrated by the work of the National Bureau of Standards on air.[9] Application of the Michelson interferometer to the testing of prisms and lenses has been described by Twyman.[10]

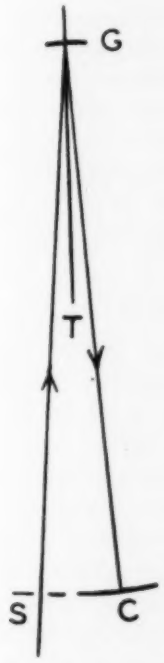

FIG. 7. Concave grating, Eagle mounting. S = slit, G = grating, C = camera, T = track.

The primary purpose of interferometers was to examine the structure of atomic radiation, and all types have been used for the investigation of hyperfine structure of spectral lines. Impetus has been given to these applications during the last decade by the quantum interpretation of hyperfine structure and in this field the Fabry-Perot interferometer has now taken the lead. Enormous resolving powers have been obtained by using highly reflecting metal films on the plates of a conventional Fabry-Perot interferometer, but these have been further increased by using two in tandem. In 1927, Houston[11] remarked that the dispersion of the Fabry-Perot interferometer is independent of the plate separation, while the distance between orders is inversely proportional to it. Thus the overlapping of orders can be avoided by using two interferometers in series, the first with small separation acting as a filter to remove some of the pattern and resulting in greater resolution than that possible with the greater separation alone. The same principle is embodied in a multiplex interference spectroscope described by Gehrcke and Lau[12] in 1930; it consists of 2 plane-parallel plates of glass or quartz of different thickness, each with semi-transparent silvering on both sides, and separated by an air gap. According to Lau and Ritter,[13] the resolving power per order, or number of lines resolvable between 2 adjacent orders, in various types of interferometers is 30 for the echelon, 17 for the Lummer-Gehrcke, 40 for the Fabry-Perot, and 200 for the multiplex. However, no extensive use of these compound Fabry-Perot interferometers appears to have been made, possibly on account of their low light efficiency. A method of increasing either the resolving power or the intensity of the fringes as given by the conventional Fabry-Perot interferometer has been described by Machler and Fisher.[14] One of the plates is silvered to opacity and this film is then ruled with parallel slits or windows.

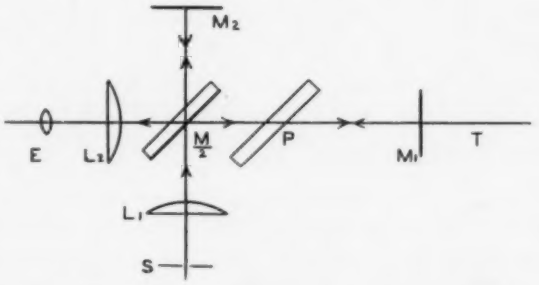

FIG. 8. Michelson interferometer. S = slit, L_1 = collimator lens, $M/2$ = semi-transparent mirror, P = compensating plate, M_1 and M_2 = mirrors, L_2 = telescope lens, E = eyepiece (or camera).

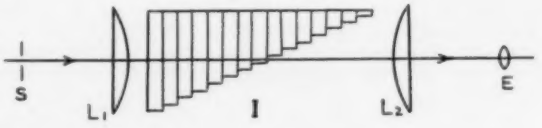

FIG. 9. Echelon interferometer. S = slit, L_1 = collimator lens, I = interferometer plates, L_2 = telescope lens, E = eyepiece (or camera).

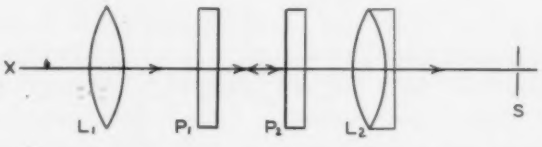

FIG. 10. Fabry-Perot interferometer. X = light source, L_1 = collimator lens, P_1 and P_2 = interferometer plates, L_2 = achromatic projection lens, S = spectrograph slit.

FIG. 11. Lummer-Gehrcke interferometer. X = light source, L_1 = collimator lens, I = interferometer plate, L_2 = achromatic projection lens, S = spectrograph slit.

3. Comparators

The numerical data of line spectra consist of wave-lengths and of relative intensities, which respectively involve comparators and photometers for their measurement. A good comparator rates far above the wave-length drums attached to constant-deviation spectroscopes and the wave-length scale that may be printed on the plate in certain models of spectrographs, both of which devices serve primarily for orientation in a spectrum. Comparators that permit one to read distances between spectral lines to 0.001 mm are built by all well-known manufacturers of precision instruments, and many spectroscopic laboratories are so equipped. However, the accurate determination of wave-lengths involves not only careful measurement but also some tedious arithmetic to transform linear distances in millimeters to wave-lengths in angstrom units, and

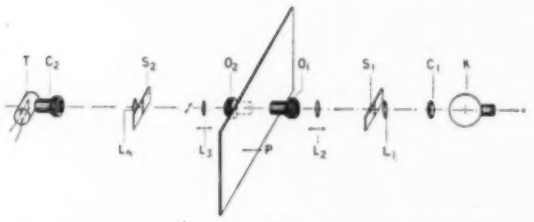

FIG. 12. Optical system of Moll recording spectrophotometer. K = lamp, C_1, C_2 = condensing lenses, S_1, S_2 = adjustable slits, L_1, L_4 = projecting lenses, L_2, L_3 = weak correcting lenses, O_1, O_2 = objectives, P = spectrogram, T = thermopile. Galvanometer and photographic recording not shown.

efforts to avoid these tasks have resulted recently in some modifications and improvements in comparators.

Thus, to expedite qualitative spectrochemical analysis Hasler and Lindhurst[14] have described a dual projection comparator which projects simultaneously with any spectrogram, a master plate on which are marked a wave-length scale and index points for the sensitive lines of all detectable elements. Coincidences are looked for throughout the spectra, but no computing is necessary.

The calculation of wave-lengths from measurements of prismatic spectrograms is especially distasteful to most workers because the dispersion is not constant and the proper reduction entails relatively much labor with the Hartmann dispersion formula. Hoxton and Mann[15] have designed and constructed an instrument which, by the addition of two moving parts to the conventional form of comparator, enables the observer to read from the precision screw directly the wave-lengths that would ordinarily be computed by the Hartmann formula.

Without doubt, the last word in spectral comparators is the marvelous machine described by Harrison,[16] which in 2 minutes automatically measures, computes and records all wave-lengths of lines on a 20-inch spectrogram and simultaneously superposes a microphotometer trace which is indicative of relative intensities. The only objection to this instrument is a very high cost which effectively prohibits its duplication in many laboratories.

4. Microphotometers

Efforts to test the quantum theory of spectral line intensities and especially the demands of quantitative spectrochemical analysis in recent times emphasized the importance of relative intensity measurements and resulted in a rapid development of methods and instruments for objective photographic photometry. Such instruments substitute for the eye some energy sensitive physical device (e.g. photo-cell, thermopile) which gives galvanometer deflections proportional to the light transmitted by successive sections of a spectrogram as the latter is moved across an illuminated slit. The essential principles of an automatic photoelectric registering microphotometer were worked out somewhat prematurely by Koch[17] in 1912, but a satisfactory instrument was developed in 1921 when more sensitive photo-cells became available.[18] Similarly, Siegbahn[19] was first to construct in 1913 a recording microphotometer incorporating the thermopile, but this type[20] did not become popular until improved thermopiles appeared in 1921. By 1925 a half-dozen different recording microphotometers had been described in scientific literature and a number of instrument manufacturers were making them.*

Figure 12 gives an idea of the optical parts in a simple type of recording microphotometer.

The commercial value of spectrochemical testing and industrial control has lately dictated further modifications in microphotometers. Many

* Recording microphotometers are at present made by Carl Zeiss, Kipp & Zonen, Leeds & Northrup.

spectrographers under pressure to obtain quantitative analyses in minimum time have substituted nonrecording microphotometers for the fully automatic types because the readings for 2 lines can be directly observed in less time than it usually takes to set the self-recording mechanism in motion. As examples of these nonrecording microphotometers those described by Vincent and Sawyer[21] and by Forrest[22] may be mentioned. The modified commercial instrument at present used at the National Bureau of Standards is shown diagrammatically in Fig. 13. At the moment nonrecording microphotometers are still in the development stage but some further improvements may be expected to result in standardized instruments in the near future.*

5. *Light Sources*

For many years the conventional light sources of spectroscopy consisted of the Bunsen flame, the direct-current arc (100–220 v) the higher voltage (10,000–40,000 v) condensed spark, and Geissler tubes and electrodeless discharges for gases and vapors. But modern developments in pure and applied science have brought forth a considerable number of modifications and improvements in spectroscopic sources. Thus, the so-called hot spark operated at extremely high voltage in a highly evacuated inclosure has extended the range of spectroscopic research to bridge the gap which formerly existed between ultraviolet light and Röntgen rays. Again the hollow cathode tube introduced by Paschen for the excitation of gases and low-melting-point metals is now giving new data to many spectra. This tube consists essentially of a hollow cylindrical cathode of metal or carbon and a metal anode between which a high voltage (500–1500 v) direct-current discharge takes place in the presence of a noble gas at a few mm Hg pressure. The excitation of an element placed inside the cathode occurs chiefly as a result of collisions of the second kind with noble gas ions and is therefore limited by the gas used. It favors higher series terms of the first 2 spectra of most elements and gives sharper lines than the ordinary arc in air. The use of this source for high melting-point elements has been developed recently by Shenstone[23] and improvements were earlier introduced by Schüler[24] who first provided cooling for the cathode. Schüler tubes operated at low current with the cathode portion near liquid-air temperature to reduce the Doppler width of spectral lines have found extensive application in the study of hyperfine structure of atomic radiation. In fact the only source to surpass it in the production of narrow spectral lines is the atomic beam which has been used by Jackson and Kuhn[25] and by Meissner[26] for the investigation of hyperfine structure.

In the field of practical spectroscopy conventional flames, arcs and sparks have been used successfully for making quantitative analyses but in the last years many modifications have been proposed with claims of various advantages. Thus an interrupted arc is recommended[27] because it prevents overheating of the electrodes and gives less continuous background. For the analysis of solutions a high voltage (2200v) alternating-current arc has been preferred by some.[28] Certain advantages are claimed for the use of high frequency sparks,[29] and others for the use of a controlled spark often referred to as the Feussner spark.[30] The electrical circuits of the conventional and of the controlled spark are shown in Figs. 14 and 15. The only real difference between the two is that the discharge circuit of the latter contains a mechanical interrupter which restricts flow of current in the spark gap to

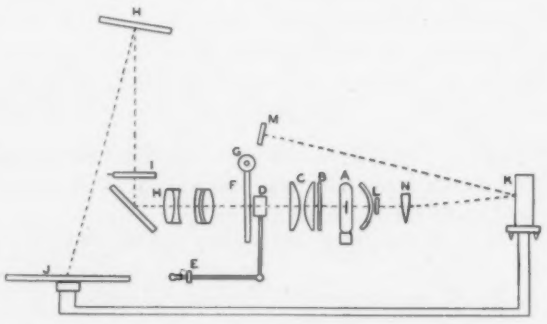

FIG. 13. A nonrecording microphotometer. A = lamp, B = heat-absorbing glass, C = condensing lenses, D = color filter, E = adjustment rod for filter, F = spectrogram rack, G = control for moving spectrogram, $H-H$ = projecting lenses and mirror, I = iris diaphragm, J = screen and photronic cell, K = galvanometer, L = reflector and target, M = scale, N = decentered lens.

* Nonrecording microphotometers are now made by Carl Zeiss, Adam Hilger, Bausch & Lomb, Applied Research Laboratories.

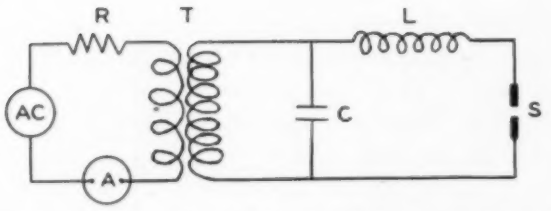

FIG. 14. Conventional condensed spark. A = ammeter, AC = alternating-current generator, R = adjustable resistance, T = transformer, C = condenser, L = self-inductance, S = spark gap.

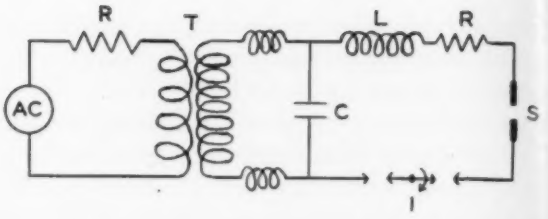

FIG. 15. Controlled or Feussner spark. AC = alternating-current generator, R = resistance, T = transformer, C = condenser, I = mechanical interrupter, S = spark gap.

instants when the condenser reaches maximum charge during each half-cycle. In this connection a discussion of characteristics of spectroscopic light sources by Sawyer and Vincent should be consulted.[31]

A recent development with promise is seen in attempts of certain makers to build a source apparatus that provides a variety of controlled excitations.

That innumerable workers employing an almost endless variety of observing conditions, succeed in making quantitative spectrochemical analyses is explained by the fact that all such measurements are relative. In each and every case the determination must be based on comparisons with spectra of chemically analyzed or prepared standards of comparable composition and any source which is reasonably reproducible for standards and unknowns can be made to yield quantitative results. Obviously the accuracy of such relative measurements increases with highly reproducible observing conditions, but it can only approach and never exceed that of the standards upon which it is based.

Bibliography

1. H. G. Gale, *Zeeman Verhandelingen* (1935), p. 280; R. W. Wood, Nature **140**, 723 (1937).
2. G. R. Harrison, *Proc. 5th Summer Conference on Spectroscopy and its Applications* (John Wiley & Sons, 1938), p. 31.
3. G. H. Dieke, *Proc. 6th Summer Conference on Spectroscopy and its Applications* (John Wiley & Sons, 1939), p. 71.
4. M. F. Hasler and R. W. Lindhurst, Metal Progress **30**, 59 (1936).
5. W. F. Meggers and K. Burns, Sci. Pap. Nat. Bur. Stand. **18**, 191 (1922).
6. W. S. Baird, *Proc. 6th Summer Conference on Spectroscopy and its Applications* (John Wiley & Sons, 1939), p. 80.
7. W. Kösters, Zeits. f. Feinmechanik, u. Präzision, **34**, 55 (1926).
8. C. G. Peters and H. S. Boyd, Sci. Pap. Nat. Bur. Stand. **17**, 677 (1922).
9. W. F. Meggers and C. G. Peters, Sci. Pap. Nat. Bur. Stand. **14**, 697 (1918).
10. F. Twyman, Phil. Mag. **35**, 49 (1918). Trans. Opt. Soc. London **22**, 174 (1921); **24**, 189 (1923).
11. W. V. Houston, Phys. Rev. **29**, 478 (1927).
12. E. Gehrcke and E. Lau, Zeits. f. Physik **63**, 313 (1930).
13. E. Lau and E. Ritter, Zeits. f. Physik **76**, 190 (1932).
14. R. C. Machler and R. A. Fisher, J. Opt. Soc. Am. **25**, 315 (1935).
15. L. G. Hoxton and D. W. Mann, J. Opt. Soc. Am. **27**, 150 (1937).
16. G. R. Harrison, J. Opt. Soc. Am. **25**, 169 (1935).
17. P. P. Koch, Ann. d. Physik **39**, 705 (1912).
18. F. Goos, Zeits. f. Instrumentenkunde **41**, 313 (1921).
19. M. Siegbahn, Ann. d. Physik **42**, 689 (1913).
20. W. J. H. Moll, Proc. Phys. Soc. London **33**, 207 (1921).
21. H. B. Vincent and R. A. Sawyer, J. Opt. Soc. Am. **27**, 193 (1937).
22. J. W. Forrest, *Proc. 6th Summer Conference on Spectroscopy and its Applications* (John Wiley & Sons, 1939), p. 88.
23. A. G. Shenstone, Phil. Trans. **237**, 453 (1938).
24. H. Schüler and H. Gollnow, Zeits. f. Physik **93**, 611 (1935); H. Schüler and Th. Schmidt, Zeits. f. Physik **96**, 485 (1935).
25. D. A. Jackson and H. Kuhn, Proc. Roy. Soc. **A165**, 303 (1938).
26. K. W. Meissner and K. F. Luft, Ann. d. Physik **29**, 698 (1937); K. W. Meissner, Ann. d. Physik **31**, 505 (1938).
27. W. Gerlach and K. Ruthardt, Zeits. f. anorg. Chemie **209**, 337 (1932).
28. O. S. Duffendack and K. B. Thomson, Proc. Am. Soc. Testing Mats. **36 II**, 301 (1936).
29. W. Gerlach and E. Schweitzer, Zeits. f. anorg. Chemie **195**, 255 (1931).
30. O. Feussner, Zeits. f. tech. Physik **13**, 573 (1932); H. Kaiser and A. Wallraff, Ann. d. Physik (5) **34**, 20 (1939).
31. R. A. Sawyer and H. B. Vincent, *Proc. 6th Summer Conference on Spectroscopy and its Applications* (John Wiley & Sons, 1939), p. 54.

Qualitative and Quantitative Chemical Analysis by Line Emission Spectra

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IT has been recognized for nearly a century that the spectrum emitted by an atom is characteristic of that atom and of its energy condition. There is no general agreement on the question of who should be credited with the discovery of this fact, but there is little doubt that the first important application of this fundamental principle of spectrum analysis was made by Kirchhoff and Bunsen. In 1860, in the course of a study of the spectra of the alkali metals, they observed in the spectra of some of their preparations spectral lines which they could not associate with any of the known alkalis. Correctly concluding that these lines indicated the presence of unidentified atoms, Kirchhoff and Bunsen undertook the separation of the suspected new elements, and in 1861 isolated the two new alkali metals, caesium and rubidium.

This striking demonstration of the power of the spectroscope, together with Kirchhoff's explanation of the Fraunhofer lines of the sun's spectrum (1859) and the use of these lines by Kirchhoff and Bunsen to demonstrate the presence of numerous metals in the sun, called the attention of the scientific world to the possibilities of qualitative analysis with the spectroscope. It is now well recognized that the study of line-emission spectra offers one of the most sensitive and rapid methods for the detection and quantitative estimation of many of the elements in solids, liquids and gases. Spectrographic methods are free from many of the sources of error and inaccuracy of chemical methods, but the practice of spectrum analysis requires a recognition of the limitations and possibilities of the method, as well as of the precautions to be observed in its application.

Although the presence of the spectral lines of an element are an indication of the presence of that element in the emitting light source, the positive identification of the spectral lines requires a consideration and elimination of the possibility of disturbing lines, i.e., lines of other elements very close to the position of the lines in question. And the converse statement, that the absence of the spectral lines of an element permits the conclusion that the element is absent from the emitting source, requires a knowledge of the excitation possibilities of the element in the source used, as well as some information on the excitation probabilities of its various spectral lines and on the sensitivity of the spectroscopic apparatus used.

That the question of disturbing lines may be very troublesome can be readily appreciated from the fact that the Harrison list[1] of the stronger spectral lines of the elements in the range 10,000A – 2000A contains 100,000 lines, or an average of about 12 lines per angstrom unit. Clearly, even if the precision of the lists and of the measurements of a qualitative determination were adequate, only the dispersion of a large grating could fix, with sufficient certainty, the wave-length and origin of a single line. Other criteria must be applied.

One such criterion is found in the lists and charts of the most sensitive lines of the elements, i.e. the lines which appear in the spectrum when only minimum amounts of the element are present in the source. Such charts are, for example, those of Bardet[2] for prismatic spectra, and of Crook[3] for grating spectra. Or one may prepare his own by marking the lines on a spectrogram recorded on his own equipment from a sample of the R.U. powder of A. Hilger, Ltd., which contains traces of fifty metallic elements.

Given an unknown specimen to investigate, the first step is to photograph its spectrum, using a light source and spectrograph adapted to the quantity and nature of the sample. It is usually desirable to record a reference spectrum beside

the unknown one, and iron is usually best, since it is so used in both charts mentioned. If the matrix, or major component, of the specimen is known or easily identified, good practice is to compare, if possible, the spectrum of a pure sample of this material, taken under identical conditions, with that of the specimen. Elimination of the common lines reduces the problem to that of the determination of the source of the remaining lines. A comparison may then be made with the reference chart of sensitive lines, and will doubtless reveal several close coincidences with lines of one or more elements. In many cases some knowledge of the sample under investigation will aid in deciding whether the presence of any or all of these elements is probable. In any case, further verification must be sought in the form of additional lines of the elements in question. Spectra of pure samples are of some use, but more helpful are lists or charts showing the order of disappearance, with diminishing amount, of the lines of the elements. Such a chart is that of Löwe,[4] showing spectra from a small quartz instrument of 1, .1, .01, and 0.001 percent of each of 44 elements, in solution on graphite electrodes; while tables with similar information are those of Twyman and Smith.[5] If all, or nearly all, of the lines which should accompany a tentatively identified line of an element are found with proper relative intensities, the presence of the element may be considered established. Similar corroborative evidence may often be gained from a consideration of the classification of the lines of a particular element. If all the lines of a multiplet or line group appear, or if the earlier members of a series are found accompanying tentatively identified lines which are higher members of the series of an element, again one may be confident of its presence.

Sometimes, however, the major constituent has a great number of lines, which obscure many of the corroborative lines sought, or it may be that there are traces of impurities in the element and it is difficult to find lines other than the most sensitive or persistent ones. Recourse must be had, then, to a process of eliminating other elements which might have radiated the lines in question. Consultation of tables of principal lines, such as the Harrison[1] or Kaiser-Ritschl[6] tables, with due consideration of the dispersion of the spectrogram, will reveal which elements have lines close enough to interfere. These elements must then be considered in turn, and their presence, or that of the one originally suspected, established. The consideration of interfering lines can be simplified by the use of the tables of Gerlach and Riedl,[7] which give, for each of the detection lines of fifty-seven elements, the interference lines which must be considered, and useful, decisive criteria for their identification.

The presence of lines of any suspected element in the spectrogram may be checked by the above procedure. The absence of the detection lines of an element indicates that it is not present in the sample in sufficient amount to be detected with the source used. It should be noted, however, that there are wide variations in the relative spectral sensitivity of different elements and of different light sources. Arcs are, in general, very much more sensitive than spark sources, and the spectra of metals much easier to excite than those of the metalloids. The gaseous elements cannot be ordinarily detected except in gas discharge tubes, and the sensitive lines of sulphur lie in the vacuum spectrograph region. Otherwise, practically every element is amenable to the ordinary methods of spectrographic analysis.

The intensity with which the spectrum of an element is excited depends, to a considerable extent, on the nature of the other elements in the sample. In general, an element of low boiling point, high vapor pressure, and low ionization potential will be excited at the expense of those of higher boiling points or ionization potentials, or of relatively lower vapor pressures at the electrode temperatures.

Under favorable conditions, the presence of an element in concentrations as low as one part in a million is readily detected. Owens[8] has reported, in the analysis of caustic liquors, an absolute sensitivity of 1×10^{-6} mg of test element on the electrodes and a relative sensitivity for manganese as low as 0.000002 percent. A rather unfavorable case, on the other hand, is that of tin in minerals, for which, having used as source the cathode layer of a d.c. arc and a glass spectrograph, v. Tongeren[9] reported a sensitivity of

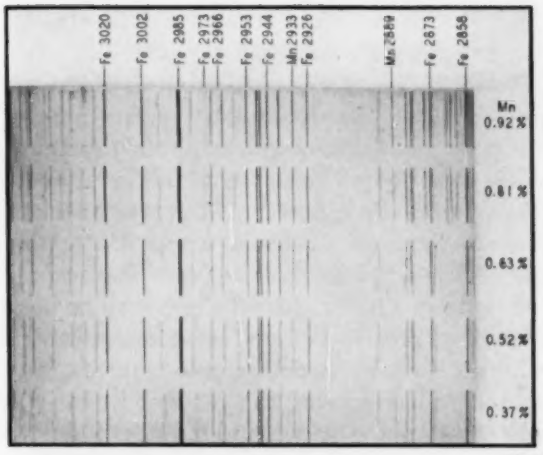

FIG. 1. Spectrograms of samples of iron, containing manganese in increasing amounts.

only 0.3 percent of SnO_2. The sensitivity in this case would have been much higher if the much more sensitive ultraviolet tin lines could have been used. Many other examples of the sensitivity of various elements in different sources are given by Owens and by v. Tongeren. Since the sensitivity of trace determination depends so much on the spectrograph, the photographic plate and the light source used, as well as on the other elements present in the sample, it is best, if previous experience in similar cases is lacking, to undertake some tests on samples of known and similar composition before reaching the conclusion that any element is lacking.

In general, under carefully selected working conditions, the sensitivity of trace analysis by the spectrograph is better than that of chemical gravimetric analysis, and as good as, or better than, colorimetric methods. The speed is usually greater, especially if suitable master charts or spectra are available. The specimens can ordinarily be used in their natural form: as solid electrodes; as liquid dried on the ends of graphite or silver electrodes; as powders or nonconductors packed in cavities in graphite electrodes. A few minutes suffice to expose and process a plate and the examination of not too complicated spectra is rapidly made.

While the qualitative examination of samples for traces of impurities is an important use of the spectrograph, no less important is the rapid spectrographic examination of samples of unknown composition to determine what elements are present and which, if any, need to be determined by the more laborious chemical methods. In this connection we may mention the sorting of scrap steels as to alloy type in steel mills,[10] the classification of minerals,[11] and the detection of metallic poisons in criminal investigations.[12]

Examples of this sort could be multiplied, but those given will serve to show that the variety of such applications is as great, perhaps, as in qualitative chemical analysis. The great advantage of the spectrograph in this type of analysis lies in its speed and the wide variety of samples which can be handled with the same equipment and technique. An exposure can be made in about a minute after preparing the sample; the photographic plate can be processed and dried in from 5 to 15 minutes; and the examination can be made in a few minutes more. Much time may often be saved in later chemical analysis by the knowledge thus gained of what elements are present.

In the analyses just discussed, the great advantages of the spectrograph, as we have seen, are its speed and universality. In connection with the trace analyses, mentioned earlier, it was pointed out that the extreme sensitivity of spectrographic determinations permitted the detection of impurities difficult or impossible to demonstrate chemically. These applications of the spectrograph are the earliest and the best known. They are today still the commonest analytical uses of the spectroscope. Quantitative analysis with the spectrograph, however, is rapidly increasing and, with further development of the technique and wider appreciation of its possibilities, bids fair, in the future, to become the most important analytical use of the spectrograph.

Quantitative spectrochemical analysis rests on the observation that when an element is present in a matrix, or body of other materials, in small and decreasing amounts, its spectral lines grow gradually weaker and disappear in a definite order. An example of this effect of abundance on the strength of the spectrum of a substance present in small amounts is seen in Fig. 1, which shows a series of iron spectra containing small known percentages of manganese. It will be seen that different manganese lines disappear with

different rates and at different percentages in the sequence. The first systematic study of this effect was made by Hartley, at Dublin, in 1882. He laid the foundations of quantitative analysis by the spectrum, and he made the first quantitative analysis—that of beryllium in cerium compounds.

Hartley and his immediate successors, such as Pollock, at Dublin, and de Gramont, at Paris, made their analyses by comparing the spectra of their samples with those of a graded series of similar composition and choosing, visually, the known which best matched the unknown. As has been pointed out above, the intensity of the spectral lines of a minor or secondary component in a source are influenced, not only by the characteristics of the spectrographic equipment and photographic technique, but also by the nature and amount of other elements in the source and by random fluctuations in the operation of the source. Accordingly, methods of visual comparison, especially without careful selection and control of the source, can be expected to give results with only the roughest kind of accuracy—perhaps 10–25 percent.

Present practice in quantitative spectrochemical analysis attains, as we shall see, an accuracy comparable with that of chemical analysis and a speed much greater. Success has followed from a careful scrutiny of every step of the process, which has resulted in more consistent and controllable light sources, better photographic materials, more direct comparison methods, and, above all, precise photometry of spectral line intensities.

The ideal light source for analytical spectroscopy would be one in which the spectral lines of each element in the electrodes varied in intensity with concentration according to an invariable and definite law, regardless of what other elements were present. If such a source were available and its characteristics well enough known, it would be possible to set up an absolute, or nearly absolute, method of analysis. A calibration of the spectrographic apparatus and photographic materials used could be made for each element by the use of one sample containing a known amount of the element. With the constants of the equipment thus fixed, later analyses could be made by a determination of the intensity with which the analysis line of the element was radiated from any sample.

Absolute spectrochemical analysis is the ultimate goal of spectroscopists; recent improvements in light sources, and photographic materials offer some hope that this goal is not unattainable. Few, however, have as yet undertaken analysis on this basis. A recent attempt is that of Preuss[13] in mineral analysis. The accuracy was quite rough but the principle may be useful when more precise methods are not applicable.

In all present spectroscopic sources, to a greater or less extent, the relative intensity of lines of any one element, and of lines of different elements, varies from instant to instant, for a variety of reasons. For example, fluctuations in discharge temperature, due largely in electrical discharges to current variation, result in fluctuation in the relative excitation of different lines because of their different excitation functions. The potential gradient in an electrical discharge depends on the ionization potential of the atoms present and so may be influenced by the kind and amount of atoms present other than those under analysis. Again, the rate and order in which different elements evaporate from the electrodes and appear in the radiation from the source depends on their relative vapor pressure and boiling points, as well as on the boiling point of the major constituent of the electrode, and is influenced by local variations in electrode temperature.[14]

The most successful quantitative spectrochemical analyses undertake to eliminate variations in the light source by the use of the "internal standard" principle of Gerlach.[15] Gerlach pointed out that many of the difficulties of source fluctuations, which are emphasized by using an "external reference standard" in another spectrum, are avoided when a chosen line of the element under analysis is compared with a line of a reference element in the same spectrum. Gerlach's original proposal was to choose, for each of several concentrations of the analysis element, a line pair made up of a line of the analysis element and a line of the reference element which were equal in intensity at that concentration. Analysis consisted of selecting visually the pair of equal intensity and thus fixing the concentration of the element to be

determined. Most modern procedures which aim at high precision use only one pair of lines. From experimental measurements a graph of the relative intensity of these lines is plotted against the concentration, and analysis is performed by reading from this analytical curve the concentration in the sample corresponding to the observed ratio of the analytical line pair.

A qualitative analysis involves the choice of a suitable light source, the selection of a spectrograph and a suitable analysis pair, and the development of a photometric technique for determining the line intensities. These three items are relatively independent of one another and so may be discussed in turn.

All spectrochemical light sources may, with scarcely an exception, be classified as flames, arcs or sparks, and each class is susceptible of more or less variation in experimental arrangement and use. The flame, as a source for quantitative spectroscopy, has been utilized chiefly by H. Lundegårdh.[16] Lundegårdh uses an acetylene-air flame into which, by means of an atomizer, the material to be analyzed is sprayed in solution. The method is especially suitable for biological analyses—such as analysis of soil, plants, and animal samples—and for readily soluble inorganic material. Lundegårdh has applied it to 34 of the commoner metallic elements. He finds a sensitivity of from 0.001 to 0.000001 mol per liter for the various elements. Higher concentrations can, of course, be handled by dilution of the solution. Suitable reference elements for the internal standard method are readily introduced into the solution. Lundegårdh states that if a photometer is used to determine the line intensities, the errors will never exceed 5 percent of the amount present and are often not more than 1–2 percent. These accuracies are as good as claimed for any other sources, but the method has not been widely adopted in this country, no doubt largely because arcs and sparks are somewhat more convenient, especially for solid samples.

The electric arc is, of all sources, the simplest in construction and operation. In essence, it requires only a connection to the direct source of potential, a regulating resistance and an arc stand to hold the samples. While its simplicity and sensitivity have made the direct-current arc popular for qualitative work, other sources tend to displace it for quantitative work because of the difficulty of obtaining an arc of steady and reproducible characteristics,[17] and because of the objectionable background usually found in the spectrograms. Some modifications of the arc are more promising. Gerlach[18] has made good use of the interrupted arc on 80 volts a.c. in which the electrodes are automatically brought together and separated. The arc is re-established at each contact; the electrodes are kept too cool for oxidization and resultant band spectra; and there is little of the wandering of the arc over the electrodes which results in erratic variations in electrode temperature and, hence, in differential evaporation of the various electrode components. A similar result is attained by Pfeilsticker,[19] who uses 220 volts a.c. across to a short gap and applies, at the peak of each cycle, a high Tesla voltage, which causes a spark to ionize the gap and permit a momentary arc flash.

An arc of analogous characteristics, but without mechanical complications, is attained by applying 1100 to 4400 volts a.c. to a gap of one millimeter or less. The voltage is sufficient to produce on each cycle an ionizing spark, which is succeeded immediately by an arc which persists until the gap voltage falls too low. The current is regulated by a large resistance or inductance in series with the arc. First introduced by Duffendack and Thomson[20] for biological analysis, it has been used by Duffendack and Wolfe[21] for caustic liquors, by Owens[8] for organic and heavy chemicals, and by Sawyer and Vincent[14] for steel. Samples may be solid metal electrodes, liquids dried on graphite electrodes or powdered material packed in cavities in graphite electrodes. Extremely sensitive, consuming a very small sample and capable of accuracy, under favorable conditions, of ± 5 percent, this source seems destined for wider use.

The most sensitive type of arc is, perhaps, that developed by Mannkopff and Peters[22] at Gottingen. They found that the radiation from the region just above the cathode in a carbon arc reveals the lines of extremely minute amounts of metallic traces in powdered samples packed in a cavity in the carbon cathode. This method has been extensively used for analysis of geo-

logical[9] and other nonconducting samples. Among the most accurate results obtained with the cathode layer are those of Preuss,[13] but this method seems to excel more in sensitivity and in applicability to refractory material than in high precision.

For samples suitable to the technique, when too great sensitivity is not required, some type of spark is preferred by many operators, because of its greater adaptability and reliability. The spark consumes a very small amount of material and the heating is localized so that erratic and differential evaporation may be lessened. A spark source operates from a transformer or other high voltage supply, generally between 10,000 and 50,000 volts, which charges a suitable condenser. The available energy is fixed by the voltage and capacity. The condenser discharges through a spark circuit containing more or less inductance and resistance and the sample gap, with an oscillating and damped current. A certain amount of inductance is needed to eliminate air lines; as more is added the discharge tends to become more like an arc in nature. The capacity used is ordinarily in the range from 0.002 to 0.2 microfarad, with inductances of 50 to 5000 millihenries. The exact sizes will be fixed by the energy available and excitation desired.

The simple condensed spark circuit has been frequently used in analysis and, as in the case of the arc, many modifications have been introduced to meet specific needs or to give improved control in operation. W. Gerlach,[18] for analysis of biological samples, has used a unidirectional Tesla discharge between a point electrode and a metal plate on which was placed a glass slide carrying the liquid or solid specimen. A similar d.c. spark has been used in biological investigations by Foster[23] and his associates at McGill University. Instead of using a Tesla discharge, however, they supplied direct current at 10 kv to a condenser, which then discharged intermittently, two or three times a second, through an inductance and the spark gap. This method is very sensitive, uses only about $\frac{1}{10}$ cc of sample, and is said to be accurate to within 10 percent.

In an attempt to regularize the damping of the trains of discharges which occur at each spark, Feussner[24] placed a synchronous motor-driven, rotary gap in the spark circuit to permit

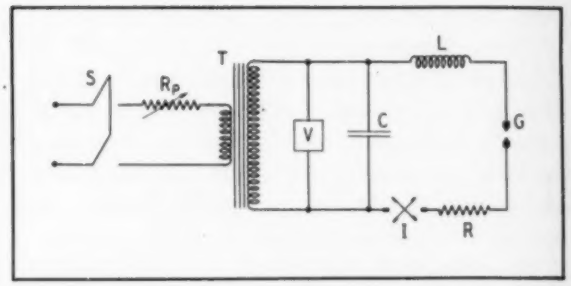

FIG. 2. Circuit diagram of condensed spark source, comprising *S*, line switch; *Rp*, adjustable primary resistor; *T*, high voltage transformer; *V*, electrostatic voltmeter; *C*, condenser; *I*, synchronous interrupter; *R*, resistor; *G*, sample gap; *L*, inductance.

sparking only at the peak voltage, and coupled inductively to the circuit a tuned circuit to absorb the energy, while a quenched gap in series also helped to damp the oscillations rapidly. Vincent and Sawyer[25] have achieved a similar result with a simpler circuit (Fig. 2) which utilizes a rotary gap but damps the oscillations by a resistance in the sparking circuit and an air blast on the spark gap. They found it possible, with this circuit, to carry out extremely rapid analyses of the composition of cast iron and steel with a probable error in a single determination of the order of 1.5–2.0 percent.

Kaiser and Wallraff,[26] in a noteworthy research on a sparking circuit of the above type, have shown the necessary conditions for reproducible sparks. Each train of sparks must die away before the next begins, so that the new series may begin always at a uniform voltage and so with the same energy available for vaporizing and exciting the electrode material, while the sparks must play over the electrode surface uniformly to avoid local effects or irregular heating. The necessary conditions for uniformity are most easily attained with circuits of the type just described, but the work of various investigators[27] has shown that excellent results may, in many cases at least, be obtained with the ordinary spark circuit.

That so many variations in light sources have been used for spectrochemical analysis is a clear indication that there is no universal source adaptable to all problems. Considerations of form and amount of sample, of sensitivity required, of speed and accuracy compel for

each new application an investigation to determine the most satisfactory light source.

Similarly, there is no universal spectrograph for all analysis work. In most of the work to date, quartz prism spectrographs have been used, largely because of the large number of sensitive analysis lines in the ultraviolet region, and because of the relatively uniform sensitivity and contrast of photographic emulsions for much of the region. Glass spectrographs are usable, especially for those elements to the left and bottom of the periodic tables, which more often have sensitive lines in the longer wave-lengths. Grating spectrographs have been less used, chiefly because in the past the lack of adequate commercial supplies has raised questions as to ready replacement of gratings in case of accident or damage in cleaning. Recently, more models of grating spectrographs have become available, and their simplicity, together with their greater dispersion and resolving power in the longer wave-lengths, should lead to their wider use, if it can be assured that their surfaces, more delicate than prism surfaces, can be adequately protected and safely cleaned.

The spectrograph should have sufficient dispersion to separate the spectral lines of the samples, preferably with a slit of 20–50 micron width, since the wide lines lead to smaller microphotometer errors. Large dispersion also tends to decrease difficulties from spectrum background, since this continuous or unresolved band radiation is diluted by more dispersion, while the line widths are unchanged. Small spectrographs generally have higher speeds than large ones, as well as lower cost, and may be preferred for use with spectra which are not too complicated.

The photographic material used for recording the spectrum should have high contrast, to give good concentrational sensitivity, and small grain size, to reduce photometer errors, and it should have uniform sensitivity and contrast over a relatively wide spectral range. Emulsions with these characteristics are generally slow. Slow speed is not necessarily a disadvantage, since adequate illumination is often available in spectrographic light sources, and it is desirable to make the exposures long enough to consume a reasonable amount of the sample. Excellent examples of fine grained, high contrast plates are the Cramer Contrast and Eastman Spectrum Analysis No. 1, both, in addition, having thin emulsions which permit rapid processing. The Eastman Polychrome plate has been much used when somewhat faster plates are needed, and has, like the other two, a wide region of relatively uniform contrast.

Plate processing is best carried out in rocking trays to promote rapid, uniform results, and to avoid Eberhard effect. Vincent and Sawyer[28] have described a technique with rocking trays and forced washing and drying by which plates with thin emulsions can be completely processed ready for photometering in from three to four minutes. Since plate processing is generally the most time-consuming step in the analysis process, some such technique is highly desirable if much analysis work is to be done.

As was pointed out above, quantitative analysis is ordinarily done by measuring the ratio of intensities of a line of the analysis element and of a reference element, and interpolating the content from a plot of this ratio against concentration of the element to be determined. For rapid work, it is essential to make the intensity measurement with a microphotometer. Numerous models of microphotometers are available and their details need not be discussed here. Nonrecording or "spotting" instruments are to be preferred, since only a few lines are to be measured and a record both consumes time and introduces an additional source of error. It is essential that the instrument be quick in action (not over one or two seconds to reach a steady deflection), and that the clear-plate and dark readings be very permanent and stable. The plate carriage must be rigid and accessible, and both the plate mounting and motion must be convenient. The instrument should be able to photometer an area at least 3 to 5 millimeters in length and 25 to 50 microns wide, in order to reduce errors due to plate grain; plate grain errors, due to random location in the emulsion of individual grains, can hardly be kept as low as a mean error of 1 percent,[29] even with fine grained plates, unless an area that large is used. With the best modern light sources and techniques, even a 1 percent photometer error will limit the accuracy of analysis.

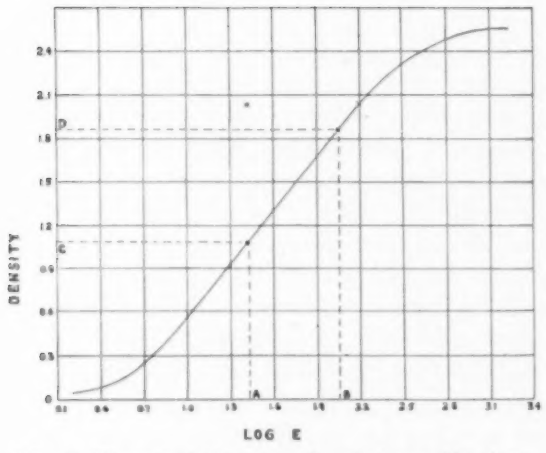

FIG. 3. Characteristic curve of a photographic plate, showing increase of density with exposure.

Numerous procedures have been developed for determining the intensity of the spectral radiations from the microphotometer readings.[30] All rest, of course, on the relationship, discovered by Hurter and Driffield, between the light exposure received by the photographic plate and the density of the developed image (Fig. 3). Since the slope of this characteristic curve of the emulsion varies from batch to batch of emulsion, as well as with age, development, and other factors, it is necessary to determine it for each plate, either directly or implicitly by determinations of intensity ratios of the analysis line pairs from spectrograms of two or more samples of known analysis recorded on the plate. Procedures which avoid direct calibration have been described by Twyman, Lothian and Dreblow[31] and by Ramb.[32]

Highest precision, however, certainly demands individual calibration and the time for such calibration need not be greater than that required by the precautions necessary in exposing and processing to avoid calibration, while the danger of error is greatly diminished. For calibration it is necessary to have on each plate a series of calibrating marks corresponding to known graded exposures. Numerous established procedures have been used to this end: Duffendack[33] replaced the spectrograph slit by a stepped slit illuminated by continuous radiation; Scheibe and Neuhäusser[34] obtained a number of graded steps of intensity in each spectral line by the use of a rotating logarithmic sector in front of the slit; Follett[35] attained the same end by an absorbing wedge before the slit. If the light source used is sufficiently uniform, a simple and time-saving method in routine work is to use several lines in the spectrum under analysis, whose relative intensities have been previously determined. This procedure has been used in steel analysis by Vincent and Sawyer.[17] In plotting the characteristic curve, some workers prefer to plot galvanometer deflection instead of density. The resulting characteristic curve is of similar general shape and usefulness.

From the characteristic curve may be read directly the exposure corresponding to the microphotometer reading or the density of any line. What is wanted, however, is the logarithm of the ratio of the exposures of the analysis and reference line. This log ratio can be obtained from the difference $A-B$, corresponding to the two galvanometer readings C and D (Fig. 3), since the difference of the logarithms is the logarithm of the ratio, and the difference is independent of the zero of either coordinate. A plot of the log concentration against log ratio for data obtained from spectrograms made under standard working conditions, from a series of samples of known graded composition, gives an analytical curve from which analyses of unknown samples may be read directly, as soon as their log ratio has been obtained from a spectrogram. Such an analytical curve for the determination of manganese in iron is shown in Fig. 4. It will be noted that the analytical curve is a straight line, as is generally the case over a considerable range of concentration. The curves, however, tend to bend over and reach a saturation as the concentration increases, thus decreasing the accuracy of determination and finally limiting the usefulness of analysis with the particular line pair. To go to higher percentages of concentration, a new line pair must be sought which saturates at higher concentration. In analysis the selection of suitable line pairs must, in fact, always be made after careful canvas of the possibilities.

Ideally, of course, the reference line should respond exactly as does the analysis line to all changes in the light source conditions; i.e., they should have the same excitation function. Actually, this ideal cannot be realized, but only more or less approximated. Experimental tests will show that some pairs of lines give results of much better accuracy than others, indicating

better parity of the lines. Line pairs which are so found to behave similarly under varying source conditions have been called by Gerlach[15] homologous lines. If possible, the reference line should be near the analysis line; proximity in wave-length avoids variation in plate contrast, while proximity on the plate minimizes variations in sensitivity from point to point of the plate. The density of the reference line should preferably fall within the working range of the density of the analysis line—generally this density range will be from 0.3 to 1.0. In the case of liquid or powdered samples, the internal standard material may be added to the sample; accordingly, a wide range of choices exists, and it is often possible to select an element with ionization potential and boiling point near those of the analysis element. Such a choice is likely to result in a satisfactory reference line the intensity of which is easily controlled by varying the amount of material added. In the case of solid samples, an attempt must be made to find a satisfactory internal-standard reference line among the lines of those constituents of the matrix which are present in large enough concentrations to preclude any effect on their line intensities due to variations in the minor constituents. Many examples will be found, in the literature cited, of suitable choices of line pairs for analysis by earlier workers.

With proper choice of analysis line pairs and of light source, quantitative spectrochemical analysis is readily carried out for all the elements for which qualitative analysis is done with the spectrograph, and for a wide variety of substances and through wide ranges of concentration. Before quantitative work can be done on a new kind of substance or element, preliminary work with graded samples of known composition is required to establish the best operating conditions and to set up the analysis curve. Once this groundwork has been done, routine quantitative determinations are made with the expenditure of little more trouble or time than is required for qualitative examination. The concentrations covered may vary from quantitative trace analyses as low as 0.00001 percent[8] to alloy compositions of 10 percent or more. The upper limit is set chiefly by the difficulty of finding suitable analysis lines that do not reach a saturation in intensity at these higher percentages. Concentrations up to 4 or 5 percent are at present the ideal range.

Recent years have witnessed remarkable improvements in the accuracy and speed with which routine analysis can be done. With proper procedure, except in very unfavorable cases, the probable error of a single observation should not be over 10 percent. Much work is regularly done with an error of 5 percent, and in favorable cases mean errors have been reported as low as 1.1 percent[36] for antimony in lead, and 1.2 percent[37] for silicon in cast steel. The error may, of course, be reduced by averaging results from several spectra, and since these may be recorded on one plate, thus involving only one plate processing, the time of analysis is not greatly extended. It should be pointed out that the error in spectrographic determinations tends to be a nearly constant percentage, whether the amount analyzed for is large or small, while the error of gravimetric chemical methods is rather a constant absolute error. The spectrographic method thus has a marked advantage at low concentrations while the chemical method is advantageous at higher concentrations.

The spectrographic methods of analysis tend to exceed chemical methods in speed, often by large factors. Many cases have been reported in which a single observer can make from thirty to fifty analyses a day, each for several minor constituents in a sample. Owens,[27] in reporting on the results of one of the largest industrial

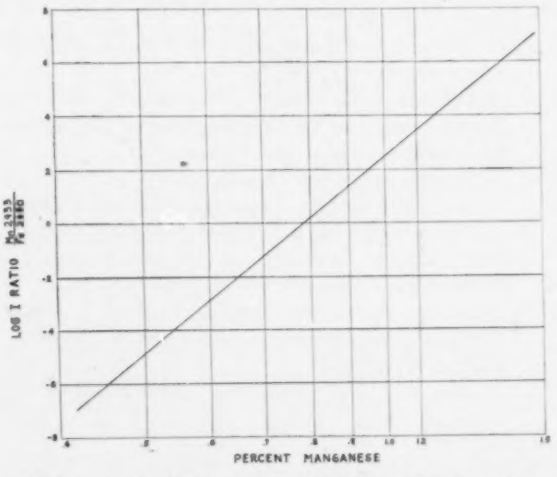

FIG. 4. Analytical curve for the determination of manganese in iron, showing increase of the logarithm of the ratio of the intensity of the manganese line, 2933A, to that of the iron line, 2880A, as the concentration of manganese increases.

spectrochemical laboratories, gives an average time required for one determination of only 7 man-minutes, while the same determinations in a chemical laboratory would take at least four times as long. Vincent and Sawyer[37] have described another large installation for iron and steel analysis in which a high precision analysis of a sample for as many as six minor constituents can be completed and reported in six minutes, and in which two crews of four operators each in a 16-hour day handle over 300 samples.

The recent progress in the development of spectrochemical analysis has led to a much greater interest and much wider application of the spectrograph to the analytical problems of biology, medicine, agriculture and industry. This increasing use of the spectrograph is strikingly shown in the rapid growth of publications in the field. In their *Index to Literature in Spectrochemical Analysis*,[38] Meggers and Scribner list the papers on the subject, by years. In the years 1920–1925 an average of 10.5 papers a year appeared, while the period 1932–37 produced an average of 107 papers a year. The art of spectrochemical analysis has reached a state where, in the ranges and for the elements and substances to which it is applicable, it can deliver routine analyses with adequate accuracy and much greater speed than the older chemical methods. There is every reason to anticipate that the active development work now being carried on will result, in the next few years, in even greater extension of the scope of the spectrograph as an analytical tool.

Bibliography

1. G. R. Harrison, editor, *Wavelength Tables* (Wiley, New York, 1939).
2. J. Bardet, *Atlas de Spectres d'Arc* (Doin, Paris, 1926).
3. W. J. Crook, *Metallurgical Spectrum Analysis* (Stanford University Press, 1933).
4. F. Löwe, *Atlas der Letzten Linien der Wichtigsten Elemente* (Steinkopff, Dresden, 1936).
5. F. Twyman and D. M. Smith, *Wavelength Tables for Spectrum Analysis* (Hilger, London, 1931).
6. H. Kaiser and R. Ritschl, *Tabelle der Hauptlinien aller Elemente* (2nd ed., Springer, Berlin, 1939).
7. W. Gerlach and E. Riedl, *Chemical Emission Spectrum Analysis* (C. Zeiss, London, 1938).
8. J. S. Owens, Ind. Eng. Chem. **11**, 59 (1939).
9. W. van Tongeren, *Chemical Composition of the Earth's Crust in the East Indian Archipelago* (Centen, Amsterdam, 1938).
10. H. Kjerrman, G. Phragmen and B. Rinman, Jernkontorets Annaler, **121** (1937).
11. O. I. Lee and T. A. Wright, *Proceedings of the Sixth Summer Conference on Spectroscopy and Its Applications* (Wiley, New York, 1939), p. 38.
12. C. W. Rankin, reference 11, p. 6.
13. E. Preuss, Zeits. f. angew. Mineralogie **1**, 167 (1938).
14. R. A. Sawyer and H. B. Vincent, *Proceedings of the Sixth Summer Conference on Spectroscopy and Its Applications* (Wiley, New York, 1939), p. 54.
15. W. Gerlach, *Foundations and Methods of Chemical Analysis by the Emission Spectrum* (Hilger, London, 1929), Chapter V.
16. H. Lundegårdh, *Die Quantitative Spectralanalyse der Elemente*, Parts I and II, Jena (G. Fischer, 1929 and 1934).
17. For example H. B. Vincent and R. A. Sawyer, J. App. Phys. **8**, 163 (1937).
18. Walter Gerlach and Werner Gerlach, *Clinical and Pathological Applications of Spectrum Analysis* (Hilger, London, 1934), Chapter I.
19. K. Pfeilsticker, Zeits. f. Electrochem. u. angew. Chemie **43**, 719 (1937).
20. O. S. Duffendack and K. B. Thomson, Proc. Am. Soc. Test. Mat. **36**, II, 310 (1936).
21. O. S. Duffendack and R. A. Wolfe, Proc. 5th Spec. Conf. (1938), p. 24.
22. R. Mannkopff and C. Peters, Zeits. f. Physik **70**, 444 (1931).
23. J. S. Foster, G. O. Langstroth and D. R. McRae, Proc. Roy. Soc. **A153**, 141 (1935).
24. O. Feussner, Arch. Eisenhüttenwesen **6**, 551 (1933).
25. H. B. Vincent and R. A. Sawyer, reference 17; Metal Progress **36**, 35 (1939).
26. H. Kaiser and A. Wallraff, Ann. d. Physik **34**, 297 (1939).
27. For example: J. S. Owens, Ind. and Eng. Chem. **10**, 64 (1938); and Barker, Proc. Iron and Steel Inst. May, 1939 meeting, in press.
28. Spectrochimica Acta, in press.
29. Unpublished results in this laboratory by H. Kaiser, H. B. Vincent and R. A. Sawyer.
30. See for example: L. S. Ornstein, W. J. H. Moll and H. C. Burger, *Objective Spektral Photometrie* (Vieweg, Braunschweig, 1932) or G. R. Harrison, J. Opt. Soc. Am. **19**, 268 (1929) and **24**, 59 (1934).
31. F. Twyman, *Spectrochemical Analysis in 1938* (A. Hilger, London, 1938), p. 18.
32. Carl Zeiss bulletin, Mess 695.
33. O. S. Duffendack, J. Opt. Soc. Am. **23**, 101 (1933).
34. G. Scheibe and A. Neuhässer, Zeits. f. angew. Chem. **41**, 1218 (1928).
35. D. H. Follett, J. Sci. Inst. **13**, 221 (1936).
36. H. Kaiser, Zeits. f. tech. Physik **17**, 227 (1939).
37. H. B. Vincent and R. A. Sawyer, Metal Progress **36**, 35 (1939).
38. Published by the American Society for Testing Materials, Philadelphia, 1939.

Absorption Spectra as Applied to Molecular Identification and Analysis

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THE "finger-print" identification system of elements, in the form of their atomic spectra, is a well-known and accepted method for the qualitative identification of many elements, and especially those of a metallic character. In recent years, considerable advance has been made in the adaptation of quantitative methods of analysis to atomic spectra, and it is now possible to estimate with considerable accuracy the amount of element present as well as the identification of the element. The accuracy of the quantitative method, from three to five percent of the amount present in the sample, may not appear to be of sufficient accuracy, and certainly is not satisfactory where the concentration of the unknown is high. However, if the unknown is present in small amounts, say of the order of 0.005 percent, then the determination of this amount with an accuracy of three to five percent of the amount present is a very satisfactory analysis. The spectrographic method of analysis does not require the separation of the unknown material from the mixture and can be applied with reasonable accuracy to samples as small as a few milligrams in weight.

In a comparatively few cases, molecular compounds, consisting of two or more elements, are capable of producing what is known as band

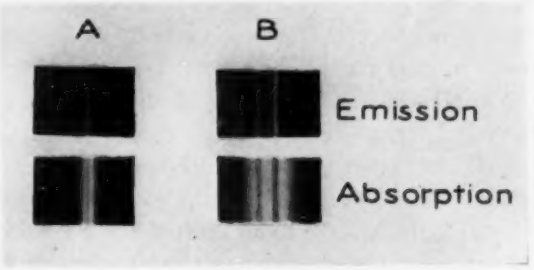


FIG. 1. Emission and reversal (absorption) effects in calcium (A) and sodium (B) spectra.

Note.—The various methods of observation of absorption spectra have been described in detail elsewhere (see Brode, *Chemical Spectroscopy*). The present article will be confined to a discussion of the significance of absorption spectra data to molecular identification and analysis. No attempt has been made here to discuss the methods of observation or recording of absorption spectrum data. For those not conversant with this field it is sufficient to point out that the combination of a suitable photometer with a spectrograph enables the operator to observe, with photographic, photoelectric, or visual methods, the spectrophotometric data required for the plotting of the absorption spectrum curve. There are available automatic recording instruments which will draw the curve as well, so that essentially all one has to do is to introduce the solution or substance in the proper position, press the proper buttons and then remove the curve from the recording drum. In general, absorption spectra data are recorded as the relative light intensity absorbed as the ordinate, and the spectral order as the abscissa. There is considerable confusion and lack of agreement among workers in the field of absorption spectra with regard to the units to record these curves. The following procedure is rather widely used and recommended.

a. Extinction.—The transmission (T) of a substance is a measure of the light intensity transmitted (I) by the material as compared to the intensity of the incident beam (I_0).

$$T = I/I_0; \quad \text{Percent transmitted} = T \times 100.$$

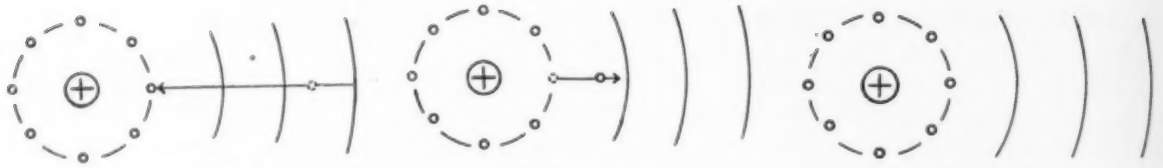
In accordance with Beer's and Lambert's laws it can be demonstrated that $I = I_0 \times 10^{-kcd}$, where k is a constant known as specific extinction, c the concentration, and d the thickness of the observed solution.

The extinction coefficient (E) can be indicated as

$$E = kcd = -\log_{10} I/I_0,$$

b. Wave-length and Frequency.—The usual method of recording visual absorption spectra is to use wave-length (λ) in millimicron units ($m\mu$), although for ultraviolet data and data including both visual and ultraviolet observations a considerable amount of published observations are recorded in frequency (ν) as fresnel units (f) (vibrations per second $\times 10^{-12}$).

The interrelation between these systems may be indicated as $1/\lambda = \nu/c$, where c = the speed of light or approximately 3×10^{10} cm per second.



(a) emission (b) absorption (c) normal state

FIG. 2. Qualitative representation of absorption and emission.

spectra when excited by the same means as used in atomic emission spectra (high temperature arc or spark). Both atoms and molecular combinations exhibit a property of absorption of light at a frequency corresponding to the emission spectra. Such absorption is known as reversal or self-absorption (Fig. 1).

From a theoretical point of view, emission spectra represents the radiant energy produced by the falling of an electron towards the proton or central nucleus, the electron having been previously pushed out of its normal level or state by the application of energy in the form of heat or electrical force (Fig. 2).

On the other hand, absorption spectra is produced in the expulsion of an electron from its normal state or level to an excited state and does not require the preliminary excitation of the molecule. This absorption excitation is produced by radiant energy, the frequency of the absorbed energy corresponding to the energy change from the normal to the excited state. Absorption thus offers a means of examination of substances without a preceptable loss of sample material and without a change in molecular structure, since the excited molecule almost always reverts to the normal state. It would seem that the necessary prerequisite for absorption would be the ability to remove electrons from the outer shell through radiation or some other exciting force. A special case, and one of extreme importance in the study of both organic and inorganic compounds, is found in those compounds in which the outer shell is complete in its octet formation but within the atom or molecule there is an incomplete shell. In such a case electrons may oscillate between their complete and incomplete shells without disturbing the completed outer configuration. This oscillation between electron forms is generally termed *resonance* and the electronic structures involved in this equilibrium or resonance are known as *electromers*.

This protected resonance may be produced within a single atom such as the rare earths (Fig. 3 a), an atom with a protecting layer of other atoms as in the case of the permanganate ion (Fig. 3 b), or a combination of two or more atoms (such as ethylene or chlorophyl) (Fig. 4).

Such resonating or vibrating groups are known as *chromophores*. In general, chromophores are those atoms or atomic combinations in which there is a deficiency of electrons so that electrons are capable of occupying more than one position

FIG. 3a. Qualitative representation of electron shift in absorption in rare earths. (Note incomplete electron shell (dotted) with protecting completed outer shell (solid).)

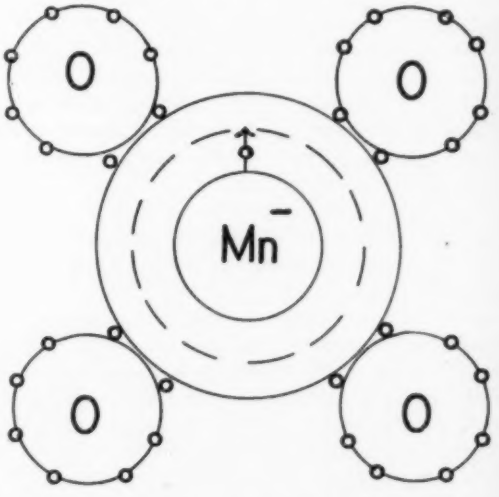
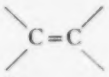
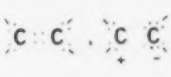
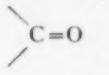
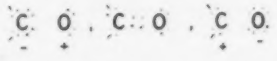
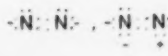
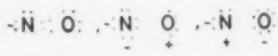


FIG. 3b. Qualitative representation of electron shift in absorption in the permanganate ion. (Note incomplete electron shell (dotted) with protecting completed outer shell (solid) formed with the oxygen atoms.)

in the molecule. Among the important chromophore groups are following:

Name	Formula	Electronic forms
Ethenylene		
Carbonyl		
Azo	$-N=N-$	
Nitroso	$-N=O$	

An important factor in the application of the chromophore theory in the prediction of the absorption spectrum or molecular structure is the combination effects of two or more chromophores. Chromophores may be in direct combination (cumulative), in alternate position (conjugated), and separated by more than one covalent bond (nonconjugated) (Fig. 5). In addition, one may alter the resonance of a chromophore by weighting groups and this alteration may affect the frequency of resonance and the amplitude of the absorption band. These changes are more specifically defined as:

(1) Bathochrome: A shift of the absorption band towards the red (lower frequency). The color deepens (i.e., a change from yellow, to red, to purple, to blue, to green).

(2) Hypsochrome: A shift of the absorption band towards the blue (higher frequency). The color lightens (i.e., a change from green, to blue, to purple, to red, to yellow).

(3) Hyperchrome: An increase in the extinction value of the absorption band. The intensity of the color increases.

(4) Hypochrome: A decrease in the extinction value of the absorption band. The intensity of the color decreases.

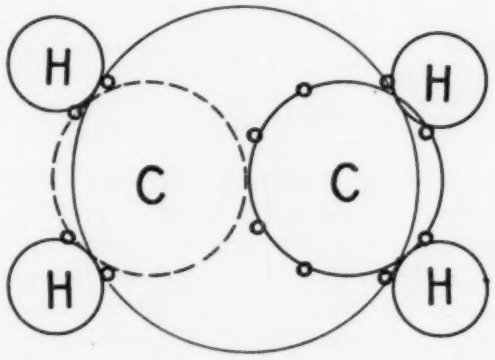


FIG. 4. Qualitative representation of electron structure in one of the resonating forms of ethylene. (Note complete octet (outer circle) with complete and incomplete carbon shells within.)

The effects of weighting groups are such as to lead one to conclude that in large and complex molecules there has been a departure from the electron type of resonance, as pictured for the simple monatomic or even diatomic resonator and that these larger and more complex reso-

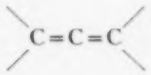
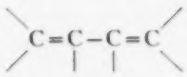
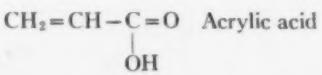
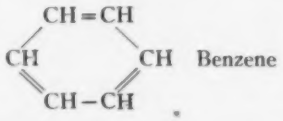
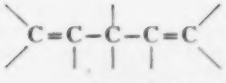
Type		Examples
(a) Cumulative		$CH_2=C=O$ Ketene
(b) Conjugated		$CH_2=CH-CH=CH_2$ 1,3-Butadiene
		 Acrylic acid
		 Benzene
(c) Separated		$CH_2=CH-CH_2-CH=CH_2$ 1,4-Pentadiene

FIG. 5. Chromophore combination.

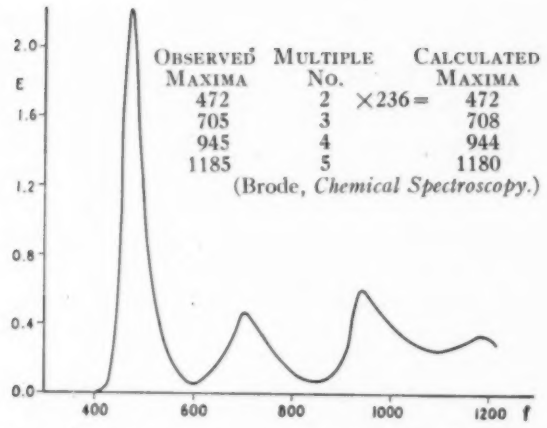


FIG. 6. Absorption spectrum of Light Green SF Yellowish (Color Index No. 670.) Fundamental Frequency = 236f.

nators conform in many ways to what would be expected from resonating or vibrating bodies.

In general, it may be said that the increase in mass of a compound results in a decrease in the frequency of vibration, although the effect is dependent in part on the position in the resonator to which the mass is attached. If the attachment to the resonating group is through an insulating atom or group there will be little if any effect. If directly attached, it may be attached in such a position as to affect the frequency only slightly, or it may cause a complete breakdown of the normal frequency, such as is produced in a vibrating sting when held or touched at a point between the two fixed ends. By attachment along the vibrating portion, or especially at the end, it may cause an increased amplitude of vibration as well as shift to a lower frequency. The comparatively simple compound, benzene, shows a complex spectrum which is resolvable into a series of uniformly spaced bands at multiple intervals of frequency corresponding to a fundamental absorption frequency in the infra-red. These components are, in themselves, resolvable, as seen in the vapor spectrum of benzene, but, on the other hand, the observation of the absorption spectrum of benzene in a solvent shows a dampening of the vibration values so that broad bands rather than line structures are observed.

The use of a polar solvent or the introduction

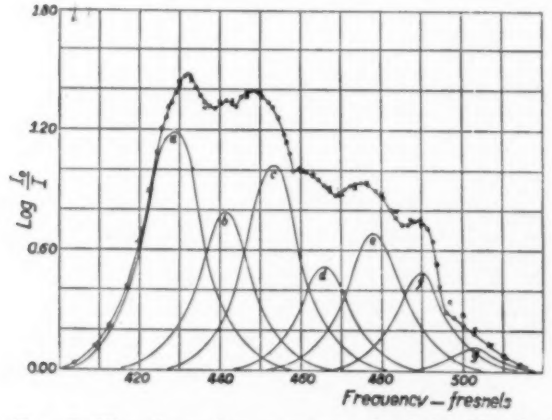


FIG. 7. The absorption spectrum of cobalt chloride in concentrated hydrochloric acid and its analysis into component bands. (Brode.)

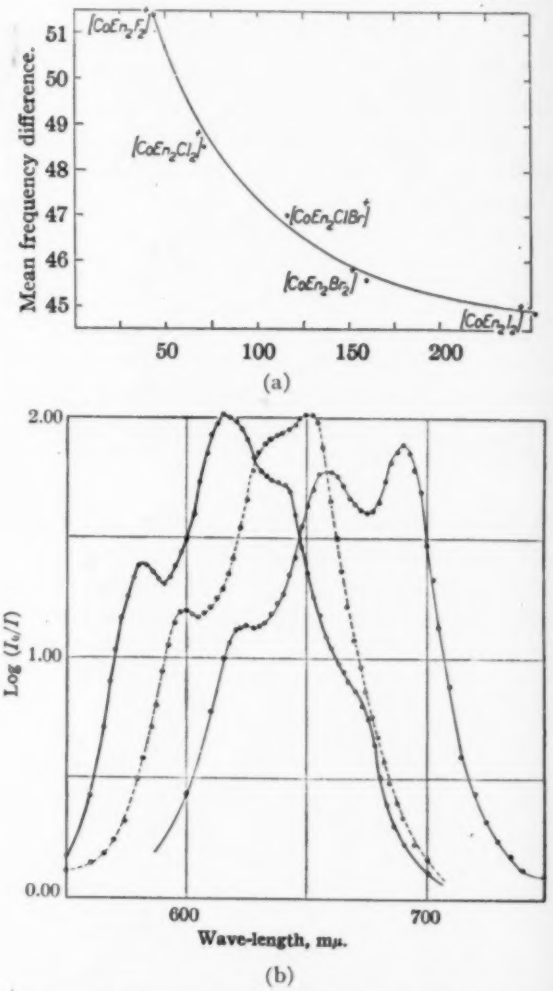


FIG. 8. Total atomic weight of halogen substituents in (1,6-series) of $(CoEn_2X_2)X$. (X = halogens.) (a) Change of frequency difference between the component bands caused by a change of the halogen substituent. (Brode and Ernsberger.) (b) Change of frequency and shift of intensities in component bands caused by change of halogen substituent. The absorption spectra of cobaltous halides in quinoline: Heavy full line, $CoCl_2$; dotted line, $CoBr_2$; light full line, CoI_2.

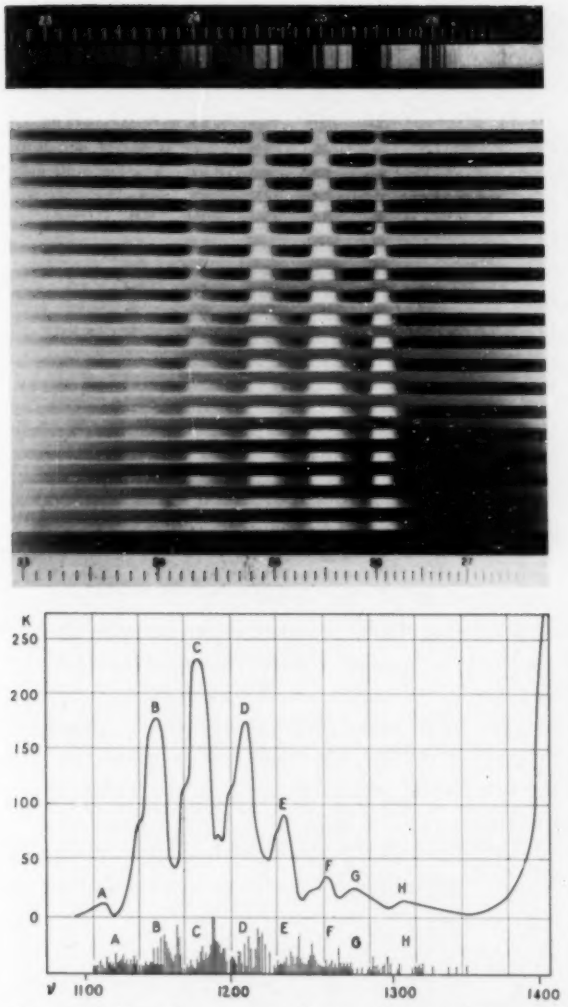


FIG. 9. Absorption spectra of vapor (upper photograph) and solution (in alcohol) of benzene (middle photograph) and graphical representation of these effects. (Brode, *Chemical Spectroscopy.*)

into the molecule of additional weighting groups results in further dampening, and eventually all indication of resolvable fine structure may be eliminated with the production of broad smooth bands. These broad smooth bands, however, may represent multiple frequency values of a fundamental frequency.

In the classification of these various band systems it appears that one may have broad bands at widely spaced frequency intervals, which may be termed *PRINCIPAL* bands. These are few in number (from one to six in the spectral range from 200 to 700 mμ) and are generally whole number or simple fraction multiples of a fundamental frequency. The lower member or members of this harmonic series are usually missing (Fig. 6).

The first apparent member of this series of principal bands is usually quite prominent, and, on increasing the number of conjugated groups in the chromophore, increasing the mass of the resonating molecule, or increasing the symmetry of the molecule, there is usually an enhancement of the first apparent member of this series as compared with the other members of the series (Fig. 7).

The *COMPONENT* bands are those which make up the principal bands. These bands do not usually appear in solution spectra as separate or resolved components but evidence themselves as inflections in the curve and in the form of an irregularly rather than a symmetrically shaped absorption band. As in the case of the principal bands, the component bands appear as multiples of a fundamental frequency, although a much smaller frequency value (e.g., 5 to 20 f).

These component bands also show a tendency for reduction of frequency and concentration of intensity of absorption in the first members of the series when the mass or conjugated character of the resonator is increased (Fig. 8).

As is shown in the vapor spectrum of benzene, the component bands, when freed of the resonance dampening effects of solvents, may be resolved into *FINE STRUCTURE* (Fig. 9). The existence of multiple relations in these fine-structure bands are not clearly indicated.

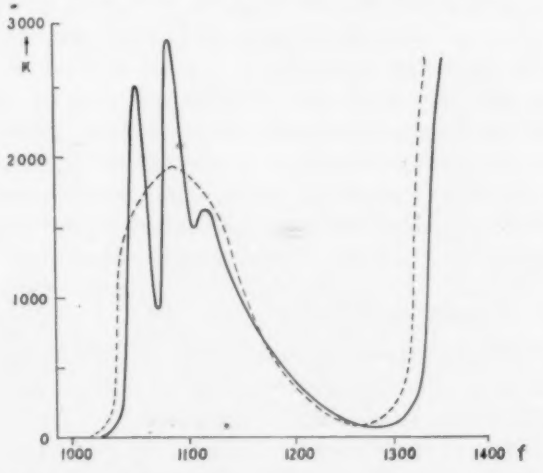


FIG. 10. Influence of solvents on absorption bands. Absorption spectra of phenol in alcohol (dotted) and in hexane (solid). (Klingstedt.) (Brode, *Chemical Spectroscopy.*)

The three types of absorption spectra bands which have been described above may be compared with the simpler band spectra which have been classified as electronic, rotational, and vibrational effects. As has been pointed out in

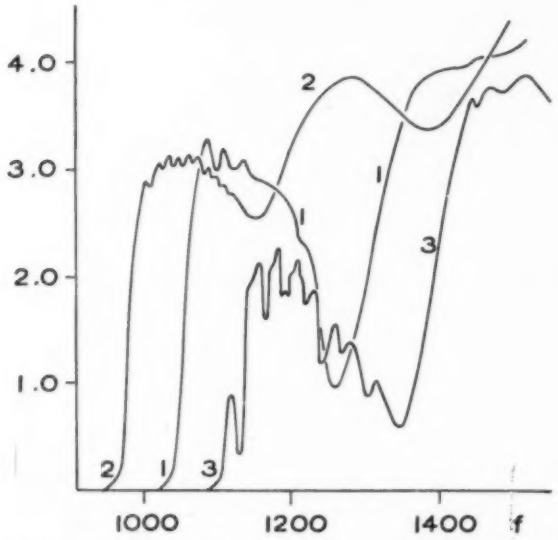


FIG. 11. Absorption spectra of benzene and substituted derivatives: 1, phenol; 2, aniline; 3, benzene. (Klingstedt-Brode from *Chemical Spectroscopy*.)

this discussion, however, there appears to be a transition from the simple types of monatomic and diatomic spectra, involving nonharmonic series of progression, to the apparent harmonic resonance of the large and complex organic and inorganic resonators which appear to vibrate as a single resonating unit.

In our discussion up to this point we have indicated the necessity of considering the dampening effects, the number and position of resonators, and the mass of the resonating groups in correlating structure to absorption spectra. We might, therefore, summarize the observed effects and indicate their application to the prediction of structure of the resonating molecule.

1. Dampening Effects

Dampening effects are evidenced by the broadening of the absorption band and the loss of component appearance of the bands.

(a) Solution Effects

The close proximity of other molecules prevents the unhindered oscillation of the resonator. Polar solvents usually produce greater dampening effects than nonpolar solvents in the presence of a nonpolar resonating nucleus (Fig. 10). On the other hand, ionic and strongly polar solvents (e.g., $CoCl_4^{--}$ in conc. HCl) (Fig. 7) often show resolvable structure, which may be explained by the surrounding of the resonating nucleus ($CoCl_4^{--}$) with ions (chloride) similar to its outer shell of atoms so that one could consider the effect of the solvent on the resonating atoms to be essentially the same as the effect of one resonator on another.

In the application of these effects one might predict the polar nature of the resonator from the change in band shape resulting from a change from polar to nonpolar solvents.

(b) Molecular Effects

Dampening of the resonance may take place within the molecule, through the attachment of weighting groups or other resonators at certain positions in the molecule. This effect may be of a dampening or resolving nature, since the added group may make the molecule symmetrical or unsymmetrical with regard to its resonating structure.

Attachment of substituents in a nonsymmetrical position may result in a broadening or

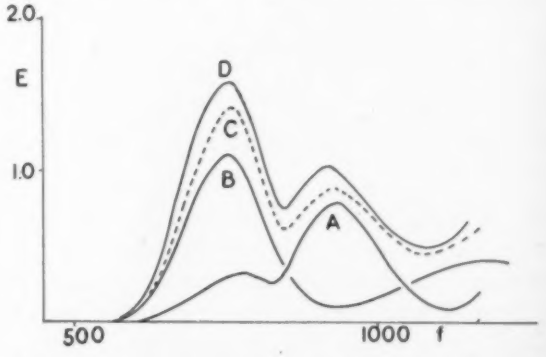


FIG. 12. Separated resonators. *A* and *B* are absorption spectra of two monoazo dyes; *C* the addition of curves *A* and *B*; and *D* the absorption spectrum of a disazo dye containing resonators *A* and *B* coupled together by an insulating link ($-CH_2-$). (Adapted from Brode and Piper.)

dampening of the resonance due to an increase in the number of resonating forms. Symmetrical attachment may cause only a greater amplitude without a change in shape although there may be additional effects and even a complete alteration

of resonance as a result of attachment of additional weighting or resonating groups (Fig. 11).

If the molecule consists of an outer shell of atoms surrounding the resonating nucleus, there will be a dimunition of the dampening effect of the solvent in proportion to the thoroughness of this protecting shell. Such linkages as $-O-$, $-CH_2-$, $-CH_2-CH_2-$ act as insulation connectors and prevent the transmission of resonance effects from one part of the molecule to another, and, if they completely surround the resonator, will act as a protecting shell. Weighting groups, which are not resonators in themselves, will cause very little if any change in the resonator if insulating connectors intervene between the weighting group and the resonator.

2. Number and Arrangement of Resonators

(a) Separated Resonators

If the resonators are in different molecules or are insulated from each other, the effect is generally that of addition of the two absorption curves of the separated resonators (Fig. 12).

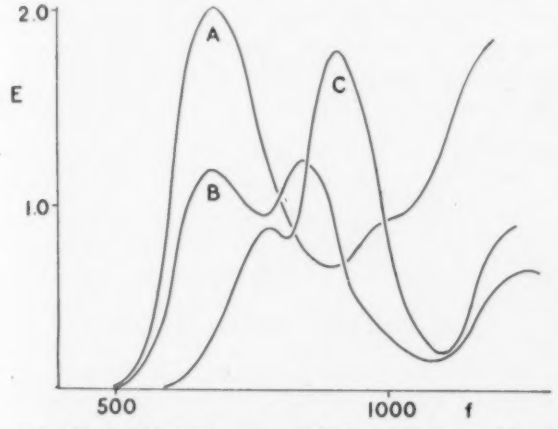


Fig. 13. Conjugated and cumulative resonators. Absorption spectra of disazo dyes, (*A*) with the two resonators conjugated, (*B*) with the two resonators cumulatively linked and (*C*) with the two resonators separated. (Brode and Piper.)

(b) Conjugated Resonators

If the resonators are directly attached to each other by a covalent linkage (single bond), the two resonators will combine to form a single larger resonator. The effect of the resonators on each other may be to counteract or repress vibration although usually the effect is to enhance (Fig. 13). The enhanced effect is usually both hyperchromic and bathochromic in character (increase in absorption intensity and shift of the band center towards higher frequency).

The combination of a number of resonators through a conjugated (vibration transmitting) linkage results in further bathochromic and hyperchromic effects, although there is a limit to the magnitude of these increases (Fig. 14). The larger resonating nuclei, unless protected sufficiently by a nonresonating layer, will become increasingly unstable as one increases the size of the resonator. This introduces an additional limit

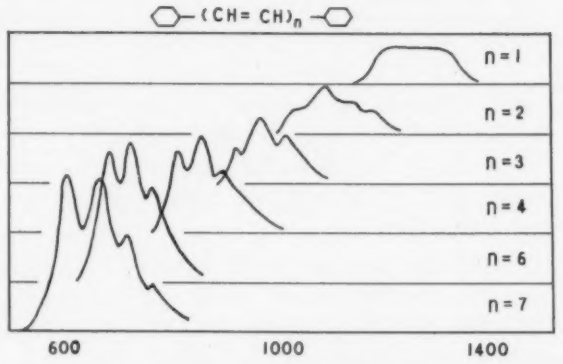


Fig. 14. Effect of conjugation in polyethenylene diphenyl derivatives. (Kuhn.) (Brode, *Chemical Spectroscopy.*)

to the effects which can be produced in the form of super-resonators.

The chemical activity of a resonating system is markedly enhanced by an increase in the number of conjugated resonators and the terminal portion of the resonator usually becomes the active or vulnerable point of the molecule (Fig. 15).

There are certain resonators, such as the benzene ring, which are unusually stable (presumably because of an endless cycle of conjugated linkages in the ring structure), and appear to have no end position. The presence of these rings at the ends of a conjugated chain promotes stability in the molecule. Another terminal group which acts as a stabilizer is the carboxyl ($-COOH$) radical (Fig. 16).

In addition to stabilizing groups there are groups which promote resonance or absorption. These latter groups are known as auxochromic groups and are sometimes classed as positive and negative auxochromes. These groups are usually attached to the benzene or stabilizing nuclei in a resonating structure. (Note: the majority of the

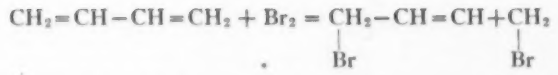
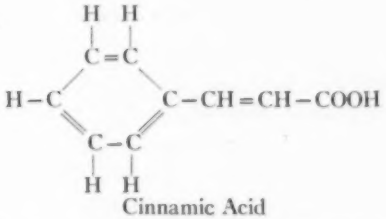


FIG. 15. 1–4 Addition to a conjugated linkage (addition of bromine to 1,3-butadiene).



Cinnamic Acid

FIG. 16. Cinnamic acid. Example of resonator with stabilizing phenyl and carboxyl groups attached to ethenylene resonator.

colored organic compounds contain stabilizing ring structures such as benzene.)

The positive auxochromes include such groups as CH_3O-, $HO-$, NH_2-, CH_3NH-, $(CH_3)_2N-$, etc.

The negative auxochromes include such groups as $-NO$, $-NO_2$, $=CO$, $-CN$, $-N=N-$, etc.

Amphoteric auxochromes include such groups as

A positive auxochrome produces an enhanced color in an acid solution, a negative auxochrome in a basic solution, and amphoteric auxochromes in either kind of solution (Fig. 17).

Since the effect of an auxochrome is to promote certain resonance effects and to act as a terminal group in the enhanced resonating system, the auxochrome must be conjugated with the resonating system.

3. *Nonresonating Substitutents*

There are a number of atoms and radicals which do not act as terminal resonators and hence as auxochromes. These groups can, however, be introduced into a resonating system at various positions in the compound and produce what might be termed weighting effects. These weighting effects are, in a sense, similar to the effect of weight application to a vibrating wire in which the position of the weight attachment will influence the total vibration and the overtone characteristics of the resonating system.

Increased mass at a definite point (especially at a nonconjugated position) produces, in general, a decrease in the frequency of vibration, just as an increase in the mass of a vibrating wire will result in a decrease in the frequency of vibration (providing the tension is kept constant). In the same example of a vibrating string or wire, a change of tension will result in a change of frequency. In a like manner there are substituent groups in the resonating molecule including both auxochromic and nonauxochromic types, which produce effects equivalent to a tension change. It is difficult to separate or differentiate between tension and weighting effects, especially where the observed physical effect is the same. The differences in chlorine, bromine, and iodine substituent effects in a resonator are not alone the effects of increased mass, but include some tension effects due to a differing electronic structure. The tension-weighting effects in this

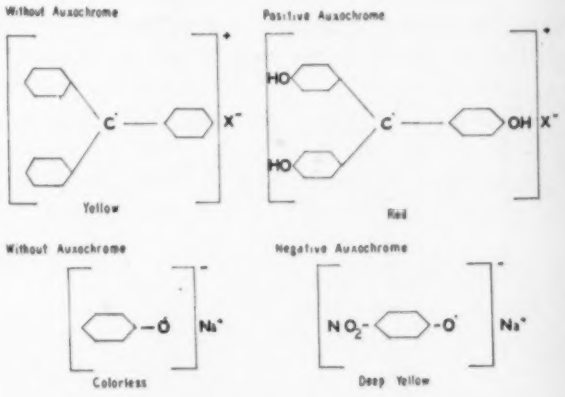


FIG. 17. Positive and negative auxochromes.

change of halogen include, in addition to a simple change of frequency due to increased mass, a change in the relative intensities of the component bands with a shift of intensity to the first principal and component bands (Fig. 18).

The tension-weighting effects are difficult to distinguish and a mere change of position of substitution may result in a change in the frequency position of the absorption band, such as might be predicted from a change in mass. An excellent example of this is found in the frequency shifts occurring in the sulfonic acid derivatives of phenylazo-α-naphthylamine and the corresponding β-naphthylamine derivatives (Fig. 19).

From these cases it would appear that an increase in the mass of the substituent may produce effects other than a mere shift of frequency, and a change of position may produce effects in frequency shift which might have been predicted as resulting from a change of mass.

By the application of the observations which has been discussed to the absorption spectra data of unknown compounds or series of compounds, it is possible to draw some rather definite conclusions with regard to the structure of the resonating substance.

A very large number of substances, both organic and inorganic in character, do not show radiant energy absorption in the photographically available region (700 to 200 mμ). Among these compounds are carbohydrates, saturated fats and oils, petroleum hydrocarbons, certain proteins, simple alcohols, ethers, salts, and acids. Many of these compounds are widely distributed in nature and form the major constituents in many plant and animal products. Their ability to transmit the radiation which is absorbed by other compounds permits the identification and estimation of many important compounds such as plant hormones and vitamins without the necessity of extraction or isolation. As has been mentioned, the production of absorption is limited in this region to compounds possessing resonators, and hence one is able at once to differentiate between those classes of compounds which do or do not possess resonating structures.

It is a rather generally accepted rule that similar (electronically similar) resonators will produce similar absorption. The application of this principle has been most effective in the prediction of the structure of unknown substances. In cases where there was some deviation in the spectra of two compounds, and especially where the deviation was that of position of band with practically identical band shapes in both cases, it has been possible to apply certain of the principles discussed concerning the effect of substituent groups as a means of predicting the difference in structure of the two compounds.

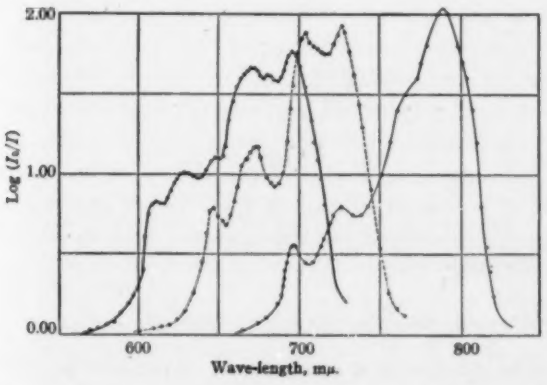


FIG. 18. The absorption spectra of cobaltous halides in their halogen acids: Heavy full line, $CoCl_2$ in HCl; dotted line, $CoBr_2$ in HBr; light full line, CoI_2 in HI.

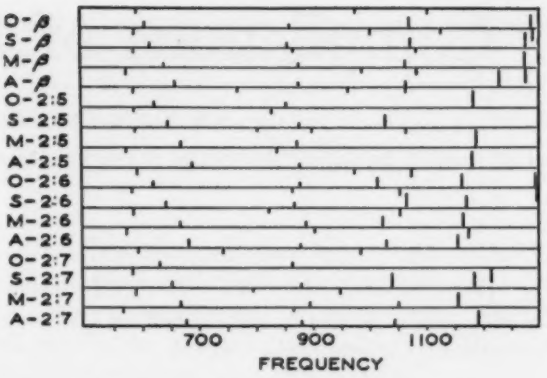


FIG. 19. Frequencies of the principal maxima of monoazo dyes derived from diazotized aniline, orthanilic, metanilic and sulfanilic acids coupled to β-naphthylamine and the indicated sulfonated naphthylamines. The length of the lines are relative measures of the intensities of the maxima which they represent. Lines pointing upward represent neutral maxima; suspended lines represent acid maxima.

Many substances, such as benzene, Vitamin A, etc. are qualitatively identified and quantitatively estimated by their absorption spectra without the necessity of removal by extraction or some other process from their natural medium or solution. The absorption spectra of resonator-containing compounds thus proves useful in the qualitative identification and quantitative estimation of compounds of known structure and properties as well as in the prediction of the structure of unknown resonators.

Acknowledgments

Acknowledgment is made to John Wiley and Sons for permission to reproduce material from *Chemical Spectroscopy* by the author of this review. For an extensive bibliography and a more complete discussion the reader is referred to this recent publication.

Compilations of Spectroscopic Data

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THE basic data of spectroscopy are the wave-lengths and intensities of the spectrum lines emitted by the atoms of the 88 known chemical elements in various conditions of excitation, of ionization, and of combination. Of the millions of spectrum lines emitted by atoms, fewer than 300,000 have been measured and listed, yet the present needs of science call for data on at least one million important lines emitted by individual atoms in their first five stages of ionization. The cataloging of atomic spectra must therefore be considered as less than one-third complete; the cataloging of the band spectra emitted and absorbed by molecules is in an even less satisfactory state.

Spectroscopic data are most frequently used, (a) for spectrochemical analysis, (b) as a means of determining excitation and ionization conditions in sources of light, and (c) by spectroscopists who are "analyzing" a spectrum—that is, determining the energy levels of an atom or molecule in a particular stage of ionization. For the purposes of none of these needs can present data be considered entirely adequate.

Spectroscopy is distinguished by the precision with which wave-length measurements can be made and hence spectrum lines identified, by the difficulty of making exact or even meaningful intensity measurements, and by the large number of investigators responsible for gathering its data. Many hundreds of papers giving spectroscopic data have been published by investigators who, in the course of their preparation of a thesis or other research, have made this single contribution to science. It is small wonder that difficulty has been found in putting on a uniform and trustworthy basis data from so many sources. Considerable order has been brought to what might otherwise be a chaotic situation by the monumental labors of H. Kayser and his co-workers in the preparation of the *Handbuch der Spectroscopie;* by the systematic studies and compilations of spectra made by Exner and Haschek and by Eder and Valenta; and by the painstaking spectroscopic measurements made over many years by such men as F. Paschen, A. S. King, W. F. Meggers, and C. C. Kiess. At the present time the most active research involving new descriptions of spectra is being carried on in America, principally at the National Bureau of Standards, the Mount Wilson Observatory, and the Massachusetts Institute of Technology.

The various compilations of spectroscopic data which are available elsewhere than in the periodical literature will be discussed under the following headings: (1) Tables for Spectrochemical Analysis; (2) Inclusive Tables of Spectroscopic Data; (3) Tables of Standard Wave-Lengths; (4) Atlases and Charts of Spectra. Original data can, of course, be found in the scientific journals. The *National Bureau of Standards Journal of Research* and the *Astrophysical Journal* are at the present time particularly rich in such material.

A bibliography of papers on the spectra of the chemical elements was published by R. C. Gibbs in 1932;[1] the recent *M. I. T. Wavelength Tables* also contain a bibliography which, though intended to contain references only for that fraction of the lines whose values were taken from the literature, will be found useful.

The most complete tables of data on band spectra in book form are probably those of Jevons; it is reported that two other British band spectroscopists are now preparing a more extensive catalog. The *M. I. T. Wavelength Tables* list approximate data on 1381 band heads frequently observed in the spectral region 10,000 to 2000A.

Tables for Spectrochemical Analysis

For qualitative analysis of materials by the emission spectrum only a few of the most

[1] R. C. Gibbs, Rev. Mod. Phys. **4**, 278 (1932).

sensitive lines of each element are usually needed, and these are most conveniently obtained from brief tables containing data for 500 or more lines. Such tables are given in the books listed in Table I. For many purposes of spectrochemical analysis more extensive tables are useful; these are listed in Table II.

Tables of sensitive lines will be found to differ somewhat from one another in detail, depending on whether they are based principally on lists

TABLE I. *Abbreviated tables for spectrochemical analysis.*

1. W. R. Brode, *Chemical Spectroscopy* (Wiley, New York, 1939). Contains a number of tables; (1) persistent lines by wave-length, listing 400 lines in the range 7950 to 1850A, given to 0.1A; (2) persistent lines by elements, with 400 lines in the range 9000 to 1600A, given to 0.1A for 71 elements; (3) principal lines by wave-length, containing about 4300 lines for the more common elements, with the gases and some other non-metals omitted, in wave-length range 8000 to 2000A, given to 0.5A, with intensity range 2 to 10; (4) principal lines by elements, containing about 6000 lines in the range 8000 to 2000A, in arc and spark, given to 0.5A, with intensity range 1 to 10; (5) spark spectrum of air, containing 300 lines in the range 7952 to 2288, given to 0.1A, with intensity range 1 to 10; (6) principal lines by elements, discharge spectrum, containing about 300 lines in the range 8000 to 2500A, given to 0.1A, with intensity range 1 to 10.
2. W. J. Crook, *Metallurgical Spectrum Analysis* (Stanford University Press, 1935). Contains 9540 lines in the range 5800 to 2780A, in the arc, for 64 elements, given to 0.1A, with intensity range 1 to 10.
3. W. J. Crook, *Table of Arc Spectrum Lines Arranged in Order of Wave-lengths* (Stanford University Press, 1933).
4. J. M. Eder and E. Valenta, *Atlas Typischer Spektren* (Hölder, Vienna, 1911). Contains about 35,000 lines in the range 7950 to 1850A, in arc, spark, and flame, for 75 elements, given to 0.01A, with intensity range 1 to 100. Contains also some bandheads. Note Rowland scale.
5. F. Exner and E. Haschek, *Die Spektren der Elemente bei Normalem Druck*, Vol. I (Deuticke, Leipzig, Vienna, 1911). Contains about 20,000 lines in several tables (not mutually exclusive), in the range 7070 to 2135A, in arc and spark, for 77 elements, given to 0.01A, with intensity range 1 to 1000. Note Rowland scale.
6. A. Gatterer and J. Junkes, *Atlas der Restlinien* (Specola Vaticana, Castel Gandolfo, Italy, 1937). Contains about 2400 lines in the range 8100 to 2200A, in arc and spark, for 30 elements, given to 0.01A. Contains also some band spectra.
7. W. Gerlach and E. Riedl, *Die chemische Emissions-Spektralanalyse*, Part III (Voss, Leipzig, 1936). Contains about 3000 lines in the range 5900 to 2140A, in arc and spark, for 57 elements, given to 0.1A. Gives control lines and possible interfering lines.
8. J. A. Hannum, "Wavelength of the Principal Lines in the Emission Spectra of the Elements," *Handbook of Chemistry*, N. A. Lange, Editor (Handbook Publishers, Inc., Sandusky, Ohio, 1937), p. 863. Contains about 5600 lines in the range 90,850 to 124A for 83 elements, with accuracy to 1A. Sensitive and ultimate lines are indicated.
9. G. R. Harrison, *M. I. T. Wavelength Tables* (Wiley, New York, 1939). Table of 500 sensitive lines of the elements, according to elements and again in wave-length order, in range 9237 to 2025A, in arc, spark, and discharge, for 85 elements, mostly given to 0.001A, with intensity range 1 to 9000.
10. H. Kayser, "Emission Spectra of Elementary Substances," *International Critical Tables*, Vol. V (McGraw-Hill, New York, 1929), p. 276. Contains about 12,000 lines in the range 350 to 31,000A, in arc and spark, for 86 elements, with precision of from 1 to 0.001A, and intensity range 1 to 10. Contains also table of air lines.
11. H. Kayser, *Handbook of Chemistry and Physics*, 20th edition (Chemical Rubber Publishing Co., 1938), p. 1476. Same as 10 above, but arranged according to elements.
12. H. Kayser and R. Ritschl, *Tabelle der Hauptlinien der Linienspektren aller Elemente*, second edition (Springer, Berlin, 1939). Contains about 27,000 lines in the range 90,850 to 33A, in arc, spark, and discharge, for 88 elements, given to 0.1 and 0.01A, with intensity range 0 to 1000.
13. F. Löwe, *Atlas der letzen Linien der wichtigsten Elemente* (Steinkopf, Leipzig, and Dresden, 1928). Table of persistent spark lines of the more important elements.
14. G. Scheibe, *Physikalische Methoden der analytischen Chemie*, Part I, W. Böttger, Editor (Akademische Verlagsgesellschaft, Leipzig, 1933), p. 67. Contains about 1100 lines in the range 7950 to 1862A, in arc and spark, for 62 elements, given to 0.01A, with intensity range 0 to 40. Includes some air lines.
15. D. M. Smith, *Visual Lines for Spectrum Analysis* (Hilger, London, 1928).
16. F. Twyman and D. M. Smith, *Wavelength Table for Spectrum Analysis* (Hilger, London, 1931). Contains a number of tables: (1) Sensitive lines in spark spectra of solutions (Hartley; Pollok; Pollok and Leonard; Leonard and Whelan). Contains about 1300 lines, arranged by elements, in the range 6725 to 2200A, for 42 elements, given to 0.1A, with intensity range 1 to 10. (2) Sensitive lines in spark spectra of solids and fused substances (De Gramont). Contains 330 lines, arranged both by elements and by wave-lengths, in the range 7948 to 2138A, for 83 elements, with accuracy to 0.1A. Most sensitive lines indicated. (3) Sensitive arc lines of 50 elements (in R. U. powder) arranged by elements. Contains 367 lines in the range 6717 to 2288A, given to 0.01A, with intensity range 1 to 10. Most sensitive lines indicated.* (4) Sensitive lines in flame spectra arranged both by elements and by wave-lengths. Contains 98 lines in the range 7699 to 2484A, for 25 elements, given to 0.1A. (5) Sensitive lines in arc and spark spectra, arranged by elements. Contains about 1000 lines in the range 7000 to 2000A, for 50 elements, given to 0.01A, with intensity range 1 to 10.
17. J. C. Boyce and J. M. MacInnes, *Wavelengths of the Extreme Ultraviolet Lines from Gas Discharges* (Palmer Physical Laboratory, Princeton, N. J., 1930). Contains about 2300 lines in the range 2500–115A, in discharge tube, for 10 elements, given to 0.01 and 0.001A, with intensity range 000 to 10. Contains air lines and some bands.
18. J. C. Boyce and H. A. Robinson, "Wave-Length Identification Lists for the Extreme Ultraviolet," J. Opt. Soc. Am. **26**, 133 (1936). Contains about 2600 lines in the range 2000 to 38A, in discharge, for 14 elements, given to 0.001A, with intensity range 00 to 50.

TABLE II. *Inclusive tables of spectrum lines.*

19. P. Auger and others, *Données Numeriques de Spectroscopie* (Gauthier-Villars, Paris, 1910–1936). Contains about 150,000 lines (including duplicates) in the range 10,000 to 2000A, in the arc, spark, flame, and discharge, for 76 elements, given to 0.1 and 0.01A, with intensity range 1 to 1000. Some bands also included.
20. F. Exner and E. Haschek, *Die Spektren der Elemente bei normalem Druck* (Deuticke, Leipzig, and Vienna, 1911). Vol. II contains about 60,000 lines in the range 6800 to 2200A, in the arc, for 67 elements, given to 0.01A, with intensity range 1 to 1000. 214 band heads also listed. Vol. III contains about 56,000 lines in the range 6800 to 2200A, in the spark, for 78 elements, given to 0.01A, with intensity range 1 to 1000. 107 bands also listed. Note Rowland scale.
21. G. R. Harrison, *M. I. T. Wavelength Tables* (Wiley, New York, 1939). Contains 109,275 lines, listed according to wave-length, in the range 10,000 to 2000A, in the arc, spark, and discharge, for 87 elements, given mostly to 0.001A, with intensity range from 1 to 9000. Air lines and some bandheads included.
22. W. Jevons, *Report on Band Spectra of Diatomic Molecules* (The Physical Society, London, 1932). Contains data on bands of 142 molecules.
23. H. Kayser, *Handbuch der Spectroscopie* (Hirzel, Leipzig). Vol. V (1910) contains about 20,000 lines in the range 39,100 to 1030A, in arc, spark, discharge, and flame, for 45 elements, A to N, given mostly to 0.01A, with intensity range 1 to 500. Contains table of air lines and also some bandheads. Note Rowland scale. Vol. VI (1912) contains about 50,000 lines in the range 8000 to 2000A, in arc, spark, discharge, and flame, for 41 elements, Na to Zr, given mostly to 0.01 or 0.001A, with intensity range 1 to 10. Also contains tables of iron lines, wave-length range 9000 to 2200A, principal lines, wave-length range 91,000 to 1850A, and bandheads. Note mostly Rowland scale.
24. H. Kayser and H. Konen, *Handbuch der Spectroscopie* (Hirzel, Leipzig). Vol. VII (Parts 1, 2, 3, 1923–1934), contains about 54,000 lines in the range 75,000 to 70A, in arc, spark, discharge, and flame for 49 elements, given to 0.01 or 0.001A, with intensity range 1 to 10. Also table of air lines. Vol. VIII (1932) contains about 22,000 lines in the range 29,300 to 250A, in arc, spark, and discharge, for 19 elements Ag to Cu, given to 0.01 or 0.001A, with intensity range 1 to 10.
25. Landolt-Börnstein, *Physikalisch-chemische Tabellen*, Ergänzungsband I, p. 336, II p. 529, III p. 763 (Springer, Berlin, 1931–1935). Contains about 10,000 lines in the range 74,360 to 291A, in arc, spark, and discharge, for 81 elements, given mostly to 0.01A. Contains also some bandheads and tables of intense and ultimate lines.
26. W. Weizel, *Handbuch der experimental Physik*, Ergänzungsband I (Akademische Verlagsgesellschaft, Leipzig, 1931). Contains data on bands of about 150 molecules.

compiled by de Gramont, Hartley, and other early experimenters; on theory; or on recent observations made with modern equipment and the new ultraviolet and infra-red emulsions of increased sensitivity. Which lines will appear strongest when vanishingly small concentrations of an element are caused to emit light will depend markedly, of course, on the type of spectroscopic equipment used, on the methods of recording and observing the spectrum, and on the type of excitation used to produce the light.

The principal lack at present in tables of sensitive lines is the failure to include lines in the long and short wave regions of the spectrum. One frequently reads that some twenty elements, including the gases and the halogens, cannot be detected spectroscopically; this misconception arises from the fact that most of the sensitive lines of these elements have wave-lengths shorter than 2000A, and that they require special methods of excitation and recording. Future tables for spectrochemical analysis may well include lines between 10,000 and 1000A, for methods of making practical analyses with equipment designed for the vacuum region are now being developed. At the present time data on important lines in the region of wave-lengths shorter than 2000A can most readily be found by consulting references 12, 17, and 18 of Table I.

Inclusive Tables of Wave-Lengths

There exist at the present time no tables of wave-lengths to which one can refer with the certainty of being able to identify *any* given spectral line whose wave-length is known to six or seven figures. Those tables which come closest to fulfilling this condition are listed in Table II. For many years Kayser's monumental *Handbuch der Spectroscopie* came closest to filling this position, but though still extremely useful, many data included in it are now markedly outdated. Though parts of Vol. 7 contain some data obtained as recently as 1934, none later than 1911 are included for some 40 elements. The *Données Numeriques* are fairly complete and up-to-date, but are somewhat inconvenient in form.

The most recently obtained data are contained in the two sets of tables (12 and 21) in which the lines have been arranged consecutively in order of wave-lengths for convenience in identifying lines. The Kayser-Ritschl tables of the 27,000 strongest lines of the elements contain data which have been selected critically from the literature to 1938, and the M. I. T. tables of the

109,000 strongest lines of the elements contain some 34,000 entries similarly selected from the literature, and 75,000 entries for literature-identified lines whose values were determined in the M. I. T. laboratories by methods similar to those discussed below. Theoretically, of course, every entry between 10,000 and 2000A in the Kayser-Ritschl tables should be found in the more inclusive M. I. T. tables, and the agreement is found to be satisfactory. An analysis of the 432 cases where disagreement is found (other than minor discrepancies to be expected because wave-length values were determined by different observers) shows the following causes assigned by M. I. T. workers:

Probable misprint in Kayser-Ritschl	33
Line in K.-R. faint on M.I.T. scale	68
Probable incorrect atom-assignment in K.-R.	56
Line in K.-R. appears only in old references, now superseded	140
Line in K.-R. not found by M.I.T. workers in available literature	135

This comparison applies only to wave-lengths and parent-atom assignments; intensities are given in the M. I. T. tables on a scale somewhat more expanded than that used by Kayser-Ritschl.

Much more spectroscopic work must be completed before entirely satisfactory tables containing wave-lengths and intensities for all important lines can be printed. There is scarcely a single complex spectrum that does not need further study before definitive tables of its lines can be produced. Several thousand new easily excited and fairly intense lines have recently been found even in an element so thoroughly studied as iron. This circumstance arises not merely from the present availability of new diffraction gratings of increased speed, and of new emulsions which make possible more thorough study of various regions of the spectrum, but of improved methods of excitation, of term analysis, and of line identification. Many of the new iron lines had been observed by previous workers, but were not recorded because of the likelihood that they might be parts of underlying band structures. Even the faintest real lines of an element are of importance to the investigator who is analyzing its spectrum, and not until a spectrum is analyzed can the best data on wave-length values and parent-atom assignments be made available. It is to be hoped that the next decade will bring a marked improvement in the data included in wave-length tables. How great this improvement will be depends to a considerable degree on improvements in wave-length standards.

Tables of Standard Wave-Lengths

The international primary standard of wave-length, Cd 6438.4696A, is correct by definition, and its value is known in terms of the standard meter to about 1 part in ten million. The International Astronomical Union has set up a number

TABLE III. *Tables of standard wave-lengths.*

27. W. R. Brode, *Chemical Spectroscopy* (Wiley, New York, 1939), p. 387. In list of principal iron lines, gives adopted secondary standards.
28. Commission 14, Wavelength Standards, Trans. Int. Astr. Union **1**, 35 (1922), contains 402 secondary and tertiary standards in the range 7032 to 3370A, for iron and neon, given to 0.001A, with intensity range 1 to 10. Trans. Int. Astr. Union **2**, 40 (1925), contains 4 neon lines in range 7537–6929A, given to 0.001A, adopted as secondary standards. Other lines listed but not adopted. Trans. Int. Astr. Union **3**, 77 (1928), contains 384 lines in the range 7535 to 3370A, in arc and discharge for iron and neon, given to 0.001A, with intensity range 1 to 10. Revision of standards, including provisional standards as well as adopted standards. Trans. Int. Astr. Union **4**, 58 (1932), contains 312 lines in range 8662 to 341A, in standard arc, vacuum arc, and discharge, for 6 elements, given to 0.001 and 0.0001A, 3 iron and 10 krypton standards adopted. Corrections to 1922 table given. Trans. Int. Astr. Union **5**, 81 (1935), contains 201 lines in the range 10,216 to 580A, in standard arc, vacuum arc, and discharge, for 7 elements, given to 0.001 and 0.0001A, with intensity range 1 to 1500. Krypton and neon standards adopted. Trans. Int. Astr. Union **6**, 79 (1938), contains 271 lines in the range 3845 to 2100A, in arc and discharge, for iron and krypton, given to 0.001 and 0.0001A, with those adopted as standards.
29. W. F. Meggers, Nat. Bur. Stand. J. Research **14**, 33 (1935). Contains 91 lines in the range 10,216 to 7164A, in the short iron arc, given to 0.001A, with intensity range 1 to 1500. Nat. Bur. Stand. J. Research **18**, 543 (1937). Contains 242 lines in the range 3497 to 2100A, in the standard iron arc, given to 0.001 and 0.0001A.
30. W. F. Meggers, *Proceedings Sixth Conference on Spectroscopy* (Wiley, New York, 1939), p. 116. Contains 346 lines in the range 7032 to 2447A, in arc and discharge, for iron, neon, and krypton, given to 0.001 and 0.0001A. Collection of all adopted secondary standards.
31. F. Twyman and D. M. Smith, *Wavelength Tables for Spectrum Analysis*, second edition (Hilger, London, 1931), p. 12. Contains 505 lines in the range 6750 to 2327A, for standard arc and discharge, for iron, helium, and neon, given to 0.001A, with intensity range 1 to 10. Collection of adopted standards and other accurate measurements.

of international secondary standards of wave-length, choosing lines which had been measured concordantly and independently in at least three laboratories. The secondary standards of iron are presumably correct to within 0.001A, while most of those of neon and krypton are known relative to each other and to the primary standard to within 0.0001A, or about 1 part in 40 million. The secondary standards, which may be found in the references given in Table III, leave little to be desired as regards precision, but are sadly lacking in number, distribution, suitability for various forms of excitation, and desirable variety of physical characteristics. An illuminating discussion of the present status of wave-length standards has recently been given by W. F. Meggers,[2] president of the commission of the I. A. U. which is charged with the responsibility for these standards.

Charts and Atlases of Spectra

In spectrochemical analysis it is often possible to eliminate any need for determining the wave-lengths of spectrum lines, by visually comparing the position of a line relative to other lines on a spectrogram with that found in a standard spectrogram produced under similar conditions. The chief drawback of this method arises from the variable dispersion produced by prism instruments, and the large number of types of prisms used. For this reason it is usually simplest for one who wishes to use charts to prepare on his own spectrograph standard plates and prints of the spectra of the most important elements. With grating equipment the problem is simpler, for the dispersion is so nearly uniform that simple magnification in a projection device serves to give any desired dispersion.

A number of atlases of spectra have been printed or are available as photographic reproductions. The more important of these are listed in Table IV. Probably the most useful of the charts are those of the spectrum of iron, since the iron lines are so frequently used for purposes of wave-length identification. Many of these iron charts have the positions of the more important lines of the other elements marked on them so that these can be identified by projection directly on the chart.

Limitations of Wave-Length Data

Despite the enormous amount of work that has been done in measuring and identifying spectrum lines, various indications show that present data are far from complete. The *M. I. T. Wavelength Tables*, though as complete as the present status of the literature will allow, appear in fact to be less than 80 percent complete even in the limited range of wave-lengths, intensities and stages of ionization which they include. The average density of lines in these tables is 14 per angstrom, and the maximum density, between 3000 and 4000A, is about 39 lines per angstrom. Fig. 1 shows the number of lines per 100 cm^{-1} (wave number units) plotted against wave-length for the range covered by the tables. While the figures used were those obtained by counting the lines in the tables, the shape of the curve would not be greatly altered if data for all known lines, including the faintest, had been used. On a probability basis one would expect that spectrum lines might, to a very rough approximation, be spaced uniformly throughout the frequency spectrum. The curve of Fig. 1, instead of being a

[2] W. F. Meggers, *Proceedings Sixth Conference on Spectroscopy* (Wiley, 1939).

TABLE IV. *Charts and atlases of spectra.*

32. J. Bardet, *Atlas de Spectre d'Arc* (Paris, 1926). Contains 54 charts of sensitive lines of the elements, with the iron spectrum, taken with a prism, from 3500 to 2500A.
33. W. R. Brode, *Chemical Spectroscopy* (Wiley, New York, 1939). Contains 35 charts for the range 5090 to 2310A, in the arc, showing the spectral lines of iron, with indicated positions of lines of other elements.
34. W. J. Crook, *Metallurgical Spectrum Analysis* (Stanford University Press, 1935). Gives 20 charts of sensitive lines of the elements in the range 5670 to 2796A, and the iron spectrum in the ranges 5671 to 5058A and 3433 to 2794A, using grating.
35. J. M. Eder and E. Valenta, *Atlas typischer Spektren* (Hölder, Vienna, 1911). Contains reproductions of over 600 photographs of flame, arc, and spark spectra, taken with glass and quartz prism spectrographs and with low-dispersion gratings. Note Rowland scale.
36. A. Gatterer and J. Junkes, *Atlas der Restlinien* (Specola Vaticana, Castel Gandolfo, Italy, 1937). Contains 28 photographs of spectra in the range 8000 to 2200A, in arc and spark for 50 elements.
37. A. Hilger, London. Charts of spectra taken with a quartz prism spectrograph, of R.U. powder (mixture of 50 elements) and of iron, copper, neon, and helium.
38. G. Scheibe and C. F. Lindström, *Tabellen des Funken- und Bogenspektrum des Eisens, etc.* (1933). Charts of arc and spark spectra, in the range 3700 to 2300A.

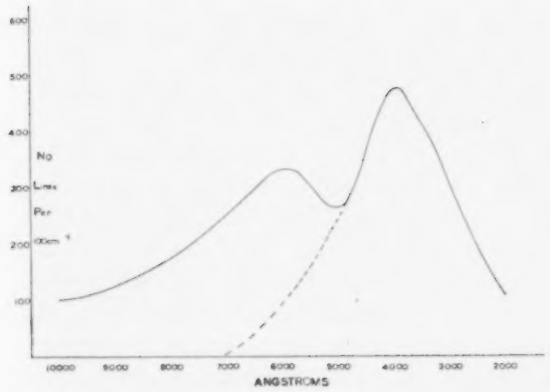

FIG. 1. The number of lines of intensity 2 to 9000 included in the *M. I. T. Wavelength Tables* per 100 wave-number units, plotted against wave-length. The dotted curve shows the probable course of the curve prior to the introduction of improved infra-red sensitive emulsions.

horizontal straight line, shows a marked peak near the region of maximum plate sensitivity. The shape of the short wave end of the curve suggests the sensitivity curve of the ordinary photographic emulsion. It seems not at all improbable that much of the area between the dotted portion of the curve, drawn in arbitrarily, and the actual curve can be credited to recent work done with infra-red emulsions of improved sensitivity. The entire curve may in the future be built up to the height of the present maximum. It should be emphasized, of course, that such statistical arguments are only approximate, for the distribution of lines is greatly influenced by chance and by the excitation conditions used in ordinary sources.

The limitations of present descriptions of spectra can be made evident in another way—by comparing the spectrum of an element such as indium, very thoroughly studied by Paschen and his collaborators, with those of the similar elements, gallium and thallium. In the M. I. T. tables 1150 indium lines of intensity greater than 2 have been listed, while for gallium only 135, and for thallium only 300, have been included. Most of the difference arises, apparently, from the lack of thoroughness with which some spectra have been studied, especially for various conditions of excitation.

Studies of such elements as ruthenium, rhodium, thorium, and uranium, and cerium and the other rare earths, show that the published descriptions of their spectra are far from complete, even for comparatively strong lines. This holds true especially in the range 2000 to 2500A, and at wave-lengths longer than 6000A, where the new aluminum-coated diffraction gratings and emulsions of improved sensitivity now bring these "underprivileged" regions nearer to parity with other regions of the spectrum. The study of complex spectra with high dispersion apparatus at wave-lengths shorter than 2000A is, of course, practically a virgin field.

Much remains to be desired, also, in regard to the precision of wave-length values. In comparatively simple spectra, lines can usually be identified if their wave-lengths are known correctly to 0.1A, and several lines can be used to establish the presence or absence of an element. In more complex spectra it often becomes important to know wave-lengths to within 0.01A, and for term analysis of a complex spectrum precision to 0.01 cm^{-1} may be desirable, which calls for wave-length precision of only ± 0.01A at 10,000A, but ± 0.0004A at 2000A.

Fortunately the broadest lines, whose wave-lengths are most difficult to determine, usually arise from the simplest spectra, while most lines emitted by such atoms as the rare earths or uranium are sharp and well defined unless hyperfine structure cannot be resolved. Sharp lines can be measured with large gratings to a precision of a few thousandths of an angstrom without difficulty, and it seems probable that with improved standards, precision to 0.001A should be not unusual.

Experience with four years of an extensive wave-length-measuring project in the M. I. T. laboratories has shown the following principal sources of error in wave-length determinations, which are here tabulated in the order of probable decreasing importance:

(1) The insufficiency of adequate wave-length standards in some spectral regions, particularly of standard lines of suitable intensities.

(2) The displacement on spectrograms of lines to be measured relative to standard lines.

(3) Displacements caused by strong neighboring lines or by blends with impurity lines or bands.

(4) The natural breadth of some lines, and the complex structure of others.

(5) Errors of coincidence, inadequately corrected for, where lines to be measured in one order are compared with standards in another order.

(6) Actual variations of wave-length with excitation conditions.

(7) Limited amounts of certain materials available for excitation to produce the lines.

(8) Incorrect identification of lines.

(9) Uncertainties of setting on line maxima.

(10) Comparator errors.

The largest errors undoubtedly come from inadequacy of the wave-length standards, with which considerable difficulty in obtaining smooth correction curves at high dispersions has been found.

Limitations of Wave-Length Standards

The iron secondary standards of wave-length range from 2447.708 to 6677.993A; those of neon extend from 5852.4878 to 7032.4127; those of krypton from 4273.9700 to 6456.291A. Spectral regions shorter than 2447A and longer than 6678 are entirely unprovided with official laboratory wave-length standards. At the present time the best that can be done for standards in these regions is to use available interferometer measurements, together with wave-lengths computed by means of the combination principle from terms which have been determined with high precision.

Even those standards of wave-length which are available leave much to be desired from several standpoints, particularly in connection with their range of intensities. The apparent wave-length of a line may vary greatly with its density on the spectrogram, when it is produced by an imperfect (i.e., actual) grating or by a reflection echelon. No matter how simple and regular in shape the spectral lines produced by a grating may appear to be in faint exposures (and gratings are almost always tested by their makers with under- rather than overexposed spectrograms) they are almost always irregular in shape when exposed to high density values. The center of gravity of the line shifts markedly with density, owing to the nonlinear character of the $d-\log I$ curve of the emulsion and the complex form of the lines produced by the grating.

It has been pointed out repeatedly by Meggers and by other experienced spectroscopists that it is impossible and undesirable to avoid overexposure of some strong lines, for frequently it is necessary to photograph at the same time many lines of widely differing intensities. Many of the iron standards are strong lines, so chosen because of the low light transmission of Fabry-Perot interferometers. They are by no means uniform in intensity, however, and when a broad region of the spectrum is covered in a single exposure, as is becoming increasingly common, it is difficult to have all standard lines of the proper density. Assuming that both standard lines and lines to be measured are narrow and simple in shape, it appears desirable that they be of equal density. The shifts produced by using some over- and some underexposed standard lines may be as great as those produced by the error of coincidences, rising sometimes to values as great as 0.02A. Such variations appear to set the chief limitation on precision of grating wave-length determinations at present.

To overcome this effect, several methods suggest themselves. One method would be to use a rotating logarithmic-sector disk to vary the intensity of all lines along their lengths, so that both standard and unknown lines could be measured at positions of optimum density. This is objectionable in that it is easy to carry out only with stigmatic grating mountings, none of which will cover a broad spectral range at one setting; also, motion along the lines which would be difficult to control during the measuring process would be required.

Another method would be to provide occulters to cover the iron spectrum, letting through only the standard lines which are to be used, and covering these in accordance with their intensities, so that very strong lines are given a short exposure, while weak lines get a much longer exposure. Such occulters are now being tested and show considerable promise.

A third method, which appears to be the most desirable, would be to provide a much greater number of working standards, whose wave-lengths should be known to 0.001A and which should have widely differing intensities. These standards could probably be provided most effectively by continuing the present system of measuring the lines with Fabry-Perot etalons.

The principal drawbacks of this method are the great amount of computation necessary to reduce fringe measurements to wave-lengths, and the uncertainties of the phase-shift corrections due to reflection at the etalon surfaces. An alternative method would be to use the quartz reflecting echelon, but this, while free from phase shift errors, and giving spectra which are simple to reduce, is perhaps even more sensitive to intensity shifts than the usual grating, and has other disadvantages. The most hopeful improvement for the provision of working standards appears to lie in the development of a device for rapid reduction of Fabry-Perot spectrograms, so that hundreds of lines could be measured in the time now required to reduce data for one. Such a machine is now under development.

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Contributors to This Issue

William Frederick Meggers received his graduate training at the University of Wisconsin and Johns Hopkins University where he received his Ph.D. in 1917. Previous to his graduate work he had served as an instructor at the University of Wisconsin and Carnegie Institute of Technology. In 1914 he became a physicist at the National Bureau of Standards becoming Chief of the Spectroscopy Section in 1919. He has served as a delegate to the International Astronomical Union for four years and was President of Commission on Standard Wave Lengths from 1935 to 1938. His contributions are to spectroscopy, atomic physics, physical optics, photography and astrophysics.

Harrison M. Randall received his Ph.D. at the University of Michigan in 1902, having completed both his undergraduate and graduate training there. Layer, he studied with Paschen, in Tübingen, and, returning to a professorship at Michigan, he became Director of the Physics Laboratories in 1917. He is the author, with Williams and Colby, of *General College Physics* (Harpers, 1937). In his special field, that of infra-red radiation, he has published many reports, including studies of atomic emission lines, molecular absorption bands, and the development of instruments and methods.

George R. Harrison received his Ph.D. degree from Stanford University, remaining at the University as an instructor until 1930. Since that year he has been Professor of Physics and Director of the Research Laboratory of Experimental Physics at the Massachusetts Institute of Technology. This year he was awarded the Rumford Medal of the American Academy of Arts and Sciences for his contributions to Spectroscopy. Dr. Harrison is the author of the recently published popular book on applied physics *Atoms in Action: The World of Creative Physics*. Dr. Harrison's picture appeared on p. 569 of Vol. 8, No. 9, 1937.

Ralph A. Sawyer received his A.B. degree from Dartmouth in 1915 and four years later completed work for his Ph.D. at the University of Chicago. During the years of 1926–27 he was a John Simon Guggenheim Memorial Fellow at the Physikalisch, Technische Reichsanstalt, Berlin, Germany with advanced study in Germany from February to August, 1931. At present he is Professor of Physics at the University of Michigan, Ann Arbor, Michigan. Dr. Sawyer's picture appeared on p. 163 of Vol. 8, No. 3, 1937.

W. F. Meggers

H. M. Randall

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After receiving his Ph.D. degree from the University of Illinois in 1925, Wallace R. Brode studied in Leipzig, Zurich, and Liverpool for two years as a Guggenheim Fellow. Since 1928 he has been with the Department of Chemistry of the Ohio State University where he is now Professor of Organic Chemistry. Dr. Brode is author of the recently published "Chemical Spectroscopy."

Infra-Red Spectra—Observation and Uses

By H. M. Randall

University of Michigan, Ann Arbor, Michigan

A nontechnical description is presented of methods of observation now in general use in infra-red spectroscopy, together with some typical examples of their use.

INFRA-RED radiation, sometimes referred to as heat radiation, comprises that region of the general radiation field which lies beyond the red end of the visible spectrum, but has not yet been extended to reach the shortest of the waves generated by purely electrical methods. This places its shortest wave-lengths at about 0.7μ while the longest measured to date are around 500μ or $\frac{1}{2}$ mm. Photographic plates are now sensitive to 1.5μ so that the spectral region of wave-lengths shorter than this is being gradually included in the field of photographic spectroscopy. In this paper we will consider those radiations lying beyond 1.5μ, which cannot be investigated by the usual photographic methods.

Such radiation has to rely for its measurement first upon the conversion of the radiant energy into heat energy, and second, the conversion of this heat energy into electrical and mechanical energy. The first of these conversions, under favorable conditions, may be quite efficient, but the second conversion is an extremely inefficient one. This is not because the proper experimental means for an efficient conversion have not yet been applied, but rather because the same inefficiency holds here as necessarily with all heat engines, of which the thermopile-galvanometer combination is one.

Since its first discovery in 1800 by Sir William Herschel, this spectroscopic region has attracted its investigators, but their number has always been small in comparison to that of those engaged in developing the photographic region or the field of x-rays. Progress has thus been correspondingly slow because of the resulting lack of concentrated effort in infra-red research. A further result of the small personnel has been that the instrument makers not finding sufficient market for infra-red equipment have not contributed so appreciably to the advancement of this type of spectroscopy as to the other fields. The infra-red spectroscopist has thus had to go his own way with comparatively little inspiration from fellow workers or help from instrument makers. In spite of these drawbacks, and the difficulties inherent in the subject itself, steady progress has been made from the first and today infra-red spectroscopy is contributing its proper share to the development of pure science and promises to become a powerful tool in industrial research.

Early investigators naturally concerned themselves with the devising of the equipment and procedures necessary to penetrate the new region. When quantitative measurements became possible, among other problems the radiation from heated surfaces was studied resulting in the production of the blackbody radiation, the explanation of whose laws, determined empirically, led to the first formulation of the quantum theory. When the time came to explain atomic spectra in terms of modern atomic theory, many of the crucial tests were supplied by infra-red measurements of the emission spectra of the elements. The accuracy and sensitivity of these measurements, if not equal to those of the data obtained photographically, were still sufficiently good to serve this purpose. As the problems of atomic spectra were approaching solution molecular spectra came on the field. Here infra-red spectroscopy has shown its greatest power to date as an instrument of research. With the gradual but continuous improvement of equipment and techniques employed, this type of spectroscopy is supreme in the field of band spectra not involving electronic transitions.

Starting with simple molecules where the bands were few and isolated and where higher resolution simply accentuated the structure of the bands, the work was gradually extended

to more and more complex molecules, such as those of organic chemistry. The spectra of these latter molecules are very complicated as would be expected considering the many kinds of vibrations and rotations possible within such complicated systems. There are at present no hopes of interpreting their spectra by the methods so successful with the spectra of the simpler molecules; further resolution but discovers more complexities of these spectra. However, it has been observed particularly with organic substances that certain lines are very often present with but small variations in their measured wave-lengths and frequencies, as one goes from one compound to another, this being true whether the material be in the solid, liquid, or vapor phase. In these compounds certain combinations of atoms are also of frequent occurrence such as the O−H, C−H and C−CH_3 groups. A correlation between these atomic combinations and the observed absorption lines just described has been made. Stating the idea very concretely "every organic radical gives rise to a characteristic series of bands, its characteristic frequencies being practically unaffected by other groups present in the same molecule or in neighboring molecules."[1] How far this idea may be profitably carried, only experience can decide. Certain of its relations, however, do appear well established and have been used effectively. Table I contains a number of such groups and their assigned frequencies.

Returning to the problem of infra-red band spectra and the use made of these spectra in the development of the theory of molecular structure, it will be evident that the more completely a spectrum may be resolved and measured the better the chances that an interpretation of the data in terms of molecular structure may be found. Beginning with the simplest molecules, diatomic, and choosing such as would have spectra of open structure, infra-red investigators have gradually proceeded from such simple molecules as HCl with a fine structure separation of 20 cm^{-1} to such complicated molecules as methyl alcohol, and to spectra where the fine structure separation is not more than 1 cm^{-1}. This progress has been achieved by appreciable improvements in apparatus and experimental techniques together with a simultaneous and corresponding increase in the power of the theoretical methods employed in the analyses. The spectroscopic arrangement[2] which the writer adopted in 1918 for the use of his students was an adaptation of that used by Langly in his measurement of the infra-red spectrum of the sun in 1880. This arrangement shown in Fig. 1, which brought the large dispersion and high resolution furnished by gratings into play in the measurement of molecular spectra has since been almost exclusively used as being particularly well adapted for work in this type of spectroscopy. It is in fact a combination of two spectrographs, a prism instrument of low dispersion, and a grating instrument of high dispersion. The function of the first is to present to the slit of the second radiation free from higher orders. The prism has accordingly a small refracting angle and its spectrum is moved across the entrance slit of the grating instrument by steps as the measurements proceed. For the far infra-red beyond 25μ where no prism material is transparent, the spectrograph,[3] Fig. 2, is limited to the grating instrument, and absorbing screens and reflecting surfaces are used to obtain pure spectra.

At present it is possible to separate sharp lines in both the near and far infra-red which are somewhat less than 0.5 cm^{-1} apart. From this it is apparent that better than this should be possible in the near infra-red; namely, in the region between 1 and 20μ where the available energy is much greater and other experimental conditions are generally more favorable.* The chief improvements in recent years may be listed as follows: (1) The introduction of the vacuum thermopile. (2) The use of amplifiers possessing amplifying factors of from 50 to 200 times. (3) The use of echelette gratings, which

TABLE I.

ν(C−H)≦3000 cm^{-1}	ν(C−C)≦ 900
ν(O−H)≦3300	$\delta(CH_2)$≦1440
ν(C=C)≦1500–1800	ν(CCl)≦ 700
ν(C−O)≦1500–1800	$\delta(CO_2)$≦ 667

* Since the above was written a letter from H. H. Nielsen informs me that he is measuring lines of water vapor from 0.25^{-1} cm to 0.3^{-1} cm apart in the region 1.5μ to 7μ.

localize the energy very largely in a narrow spectral region. (4) Improvement in the optics employed with the result that the spectral image at the emergent slit shows less distortion than formerly. (5) The increased use of vacuum spectrographs, which prevents the loss of energy by the absorption of the water vapor and carbon dioxide of the air. No satisfactory improvement in the sources has been found though the larger gratings, up to 10 by 20 inches in ruled surface, have increased the available energy many times.

In the set-up shown in Fig. 1 the source L is usually, for work in the near infra-red, either a Nernst glower or a glowbar heated to a high temperature, 800°C or more, by a suitable current. For work in the far infra-red the best source is the white-hot surface of a gas mantle, the reason being that this source is deficient in those radiations of short wave-length which comprise the impurities most difficult to remove by absorbing screens and reflecting surfaces. Unfortunately having to burn in the open air this source can be used in a very limited number of instances only. Generally a glowbar, a commercial heater unit, or platinum ribbon covered by thin layers of various materials are the most convenient, though at best form but unsatisfactory sources. Covered by powdered gas mantle material or some of the oxides composing these mantles, a better radiating surface is formed than the blank platinum surface would furnish, but not one possessing the characteristic radiation which makes the gas mantle, when heated by burning gas, so advantageous a source for far infra-red work. While hot sources are quite satisfactory for the near infra-red region, it may be possible some time to replace them to advantage if a source directly transforming electrical energy into the radiation of the long wave-length region could be devised. The reader will perceive that the source of radiation is no problem for the near infra-red region but is a vital one in the far region. An illustration will explain the situation. By using the laws of blackbody radiation as being sufficiently applicable to the radiation of our sources for this purpose, it will be found that the radiation at 100μ in a given narrow spectral region is $\frac{1}{16}$ that in a corresponding region at 50μ and at 200μ, but 1/256 that at 50μ. The reverse would be true were it possible to get a purely electrical source to emit measurable radiation at 50μ. The longer radiations would be progressively more easy to produce.

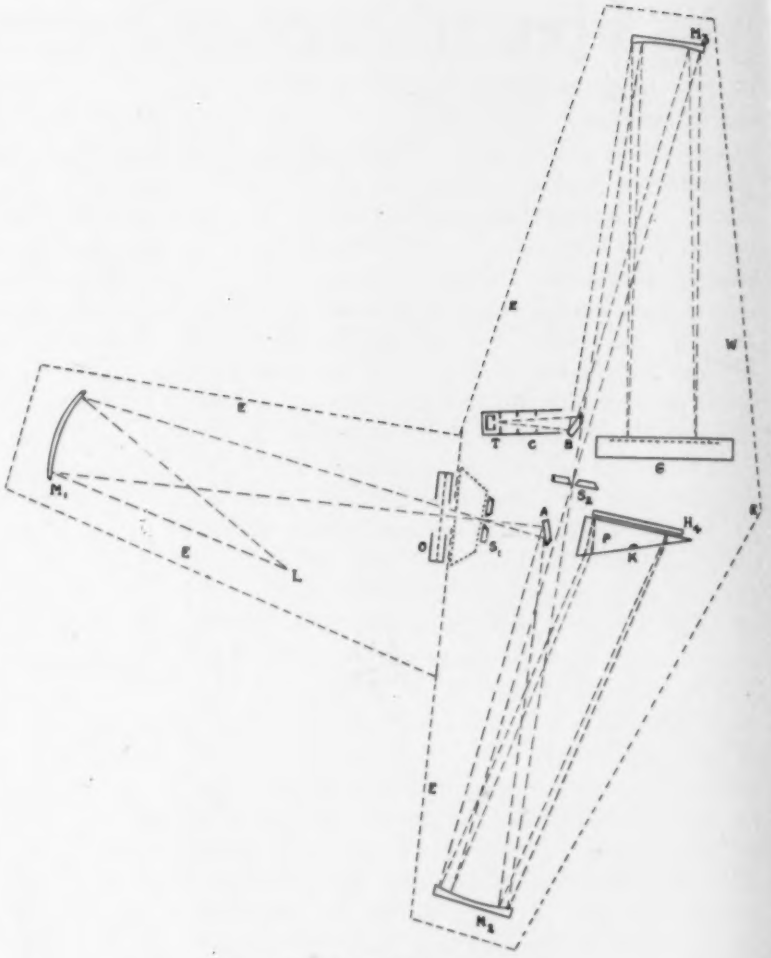

FIG. 1. Prism-grating spectrograph.

The slits S_1 and S_2 which pass the radiation into and out of the grating instrument, Fig. 2, should be adjustable in width, without changing

the constant of the spectrograph at the same time. For investigations where maximum supply of energy is a requisite long slits, possibly 2 inches, may have to be used. Here the optics of the spectrograph will produce a curvature in the slit image. As a linear thermopile is easiest made, the emergent slit should be straight. If the curvature is a function of the deviation produced by the grating, then the entrance slit must be curved and the curvature adjustable. When plenty of energy for the work is available and short slits are adequate, no questions of curvature will arise. This refinement need not be considered for the prism instrument preceding the grating.

Coming to the grating, what are the considerations which determine its choice? Generally speaking, greater dispersion and higher resolution has characterized the progress in infra-red spectroscopy; that is, a longer spectrum and a narrower strip of it, used to activate the thermopile. This process, which diminishes the energy reaching the thermopile, may be in part compensated by using larger gratings. In fact for the near infra-red, gratings now have ruled surfaces of 7×9 inches where twenty years ago the ruled surfaces were expressed in terms of about the same number of centimeters.

The first gratings used in this division of spectroscopy were gratings ruled for the photographic field. A grating with 15,000 lines per inch permits measurements to 3μ, while a grating with 5000 lines per inch would be usable to still longer wave-length regions. But these gratings generally produced a multiplicity of spectra of different orders both to the right and to the left of the undeviated image, into which image also a good deal of energy went. This dissipation of the available energy into many spectra made working with gratings much more difficult than with prisms where all the energy of a given frequency is conserved in a narrow strip of a single spectrum. This disability of the photographic gratings has been to a very appreciable extent overcome by the use of echelette gratings,[4] which approach prisms in their ability to locate radiation of a given frequency in a single spectral order. This result is achieved by ruling the grating on a soft surface, the shape of the ruling tool being such that the lines have the form of shallow V-shaped grooves, one side wide and one narrow. The narrow one, nearly normal to the grating surface is ineffective, the wider one, inclined at about 24° to the surface of the grating, is the working face of the groove. By loading the ruling tool properly the grooves, for the finer gratings, are made just deep enough to eliminate practically all of the original surface of the grating. There is accordingly very little energy reflected back into the undeviated image. Gratings with the working faces of the grooves inclined at about 24° to the grating face and with 1200 lines per inch throw the radiation at 18μ very strongly into a single first-order spectrum. Spectral regions at each side of 18μ are not so strongly localized but still permit the spectrum between 15μ and 25μ to be measured. Similarly a grating with 900 lines per inch may be made to function well on each side of 30μ, a 600-line grating around 50μ, a 360-line one around 90μ, a 133-one at 110μ and one 87.8 lines per inch at 140μ. Thus to measure the spectrum between 18 and 150μ it has required the use of six gratings, all of them having ruled surfaces of 10×20 inches except perhaps the 1200 line grating where a surface of 9×9 inches would be sufficient. Similarly in the near infra-red a collection ranging from a maximum ruling of 15,000 lines per inch to 1200 lines is required.

From the foregoing description of the workings of echelette gratings it might appear that they were as effective as prisms. This is far from being the case however. Superposed upon the first-order spectra whose conservation by the echelette grating has been stressed are also similar concentrations of all the higher orders corresponding to the first order. For the near infra-red, where transparent materials are available for prisms, the separation of these higher

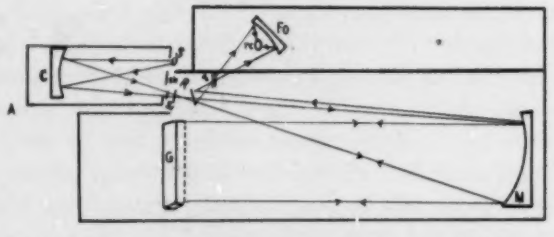

FIG. 2. Grating spectrograph for far infra-red (side view). *S*, source; *A*, absorption cell; *M*, half-parabolic mirror; *G*, echelette grating; *TC*, thermocouple.

FIG. 3. Thermopile after Weyrich.

orders presents no difficulty since the prism instrument is adjusted to present to the entrance slit of the grating spectrograph only the first order of the radiation under examination. For the far region this overlapping of higher orders constitutes a very serious difficulty. So far these orders are eliminated only by absorbing screens and suitable reflecting surfaces. At each absorption and reflection some of the first-order radiation under examination is lost along with the radiation of shorter wave-length which it is thus sought to eliminate. When sufficient purity has been attained by these methods only a small fraction of the original first-order radiation may have survived. Better methods of purifying the spectrum are urgently needed.

The large number of echelette gratings required if an extended spectral region is to be covered constitutes a decided handicap to the use of these gratings. However since work in this field has been one of the major research interests at Michigan it appeared desirable to be in a position to rule as many echelette gratings as might be necessary. A ruling engine was accordingly built. The gratings now being ruled on this ruling machine, judged by the quality of the results obtained in all the investigations carried on with them both in this country and abroad are quite adequate to meet the demands so far made upon them. No comprehensive study of the engine or of the gratings ruled by it has been made though that is desirable and may be necessary should the time arrive when the gratings become the weak member of the combination which constitutes the infra-red spectrograph.

Of the early gratings which were successful, one was ruled on a surface of a copper nickel alloy and several on aluminum surfaces. Now pure tin is used where the lines per inch number more than 2400 per inch and solder when coarser gratings are ruled. The grooves of the finer gratings are pressed out by carefully shaped diamond tools but with the coarser gratings it has been found necessary to remove the material and a cutting tool of steel is used. The solder surfaces have maintained their brightness for the length of time which has elapsed since they were first used, that is about 6 years. With the methods of evaporating films of noncorroding metals, such as aluminum or chromium, becoming constantly more accessible these solder surfaces may shortly be protected by such films. Moreover, the fixing of thin solder surfaces upon the blanks of aluminum alloy presents difficulties which also may be avoided by the evaporation of soft metals upon optically flat glass surfaces. The engine will rule gratings as fine as 14,400 lines per inch. The coarsest grating ruled so far has 25 lines per inch. The engine can undoubtedly be used to rule laminary gratings which have some definite advantages for use in the far infrared.

Returning to Fig. 1. While care was taken to have the angle between the axes of the beams incident on the concave mirrors M_2 and M_3 and the axes of the mirrors as small as possible still an

appreciable angle exists which results in some distortion of the image formed at the exit slit with a corresponding decrease in resolution. From Fig. 2 it is evident that if the parabolic mirror M were a complete mirror and the beam through the entrance slit had sufficient aperture completely to fill the mirror the axes of the beam and mirror could be made to coincide with a resulting minimum of distortion of the image formed by the mirror upon the emergent slit. This method of half-mirrors used here for some twenty years presents decided points of advantage in reducing aberration. More recently[5] the same result has been obtained by employing two parabolic mirrors reinforced by two plane mirrors mounted immediately adjacent to the slits with apertures at their centers to pass the radiations proceeding through the slits. In any case, for maximum resolution, the image distortion should be reduced to a minimum. Resolution may also be increased by lengthening the focal length of the collimating mirror or mirrors. These have been increased in the course of time from about 20 cm to one meter or more in both the near infra-red and far infra-red spectrographs.

The emergent slit S_2, Fig. 2, is made one of the foci of the elliptical mirror behind the thermopile while the thermopile surface is at the other focus. This use of elliptical mirrors has resulted in very sharp images of the emergent slit upon the thermopile receivers, reduced in size in the ratio of about four to one.

There remains to be described the thermopile which at the present time is the device most frequently used to measure the energy of the radiation in the different parts of the spectrum. The instrument is outwardly simple enough, but a good thermopile represents not only exceptional skill in the manipulation of the very small parts composing the pile but also a most careful consideration of all the numerous factors which go into the design of this instrument. Anyone seriously interested should consult one or more of the authoritative articles on the subject.[6]

Figure 3 shows a thermopile and its mounting. The receivers, upon which the radiation passing the emergent slit of the spectrometer is focused, are shown—four in number—forming a linear pile 18 mm long and 0.8 mm wide—a size determined by the operating conditions for the far infra-red. Soldered to the backs of each of these receivers, which are of very thin tin, is the thermojunction of the couple which also supports it. The cold ends of the couple are soldered to the copper plugs mounted in the lucite form above which the pile is mounted. The thermopile wires are of Hutchin's alloy (95 percent Bi−5 percent Sn and 97 percent Bi−3 percent Sb). Copper leads, soldered to the other ends of these plugs pass down the metal tube and out of a side tube near the bottom. At this point these leads are carefully cemented in the side tube and, once tight, remain so. This vertical tube, which supports the pile, ends in a ground joint which makes a vacuum seal with the copper tube leading to the pump. A metal cap, with a window of proper size, slips over the pile in its containing tube, which is half cut away for the length of the pile. The cap extends into a groove in the enlarged part and the joint is made vacuum tight with Apiezon wax. Several such caps, one with a window of KBr, one of hard paraffin, and a third of crystalline quartz are provided. The ground joint union at the end also permits the exchange of one thermopile for another with a different absorbing material on the receivers. These arrangements have been found very advantageous when long spectral regions are to be covered as they permit using the best window material and

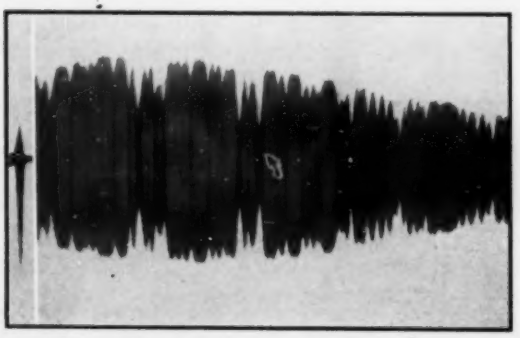

FIG. 4. The far infra-red spectrum of D_2O between 31μ and 38μ.

receiving surfaces at each part of the spectrum. A pair of wires from each couple permits joining the couples in any desired way before being soldered to the galvanometer leads. In the present case the two lower couples are joined in series in

opposition to the two upper couples in series. This method aids in preventing drifts when the shutter is built to illuminate first the upper pair, then the lower pair, as it operates. Such a couple, if properly made, will gain in sensitivity 3 to 10 times when evacuated to a pressure of 10^{-5} mm of mercury. This one will give an amplified galvanometer deflection of 400 mm, when 0.036 erg/sec. falls upon the receivers; the period of the galvanometer being 16 sec.

With the prism grating spectrometer, higher orders are eliminated by the prism but in the far infra-red various combinations of absorbing screens and reflecting surfaces have to be used to obtain pure radiation. The thermopile receivers are covered with absorbing material which varies with the part of the spectrum under examination: bismuth black in the near infra-red and Aquadag (graphite) or powdered glass for the far region. An ideal coating would be a material 100 percent absorbing in the region under investigation, and reflecting in other regions. The thermopile windows act as filters as well; the paraffin absorbs the shorter waves below 20μ more strongly than the longer ones. The crystalline quartz windows absorb between 4μ and 50μ. Filters made of films covered with antimony black of the right coarseness are opaque for the near infra-red but become good transmitters beyond 50μ.

The mirror, R (Fig. 2), may be replaced by *reststrahlen* plates of different materials which reflect copiously in the region under examination,

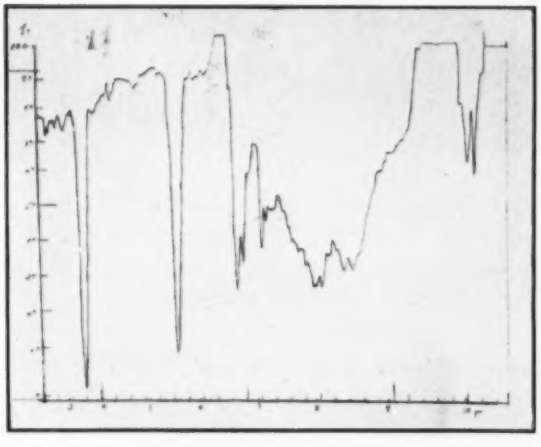

FIG. 5. The Hardy recording spectrophotometer, registering as ordinates the percentages of transmission. Region 2.5μ to 10.5μ.

and poorly elsewhere. A series of plates whose regions of reflection change by small steps between 20 and 100 are provided. Finally the shutter, which passes the radiation from the source intermittently through the entrance slit, may be transparent to the radiation suppressed and opaque to the radiation under examination—in which case the current pulses to the galvanometer are due primarily to the interruptions of the latter radiation. It has been found possible by suitable combinations of filters and reflecting surfaces to obtain sufficiently pure radiation between 20 and 140μ.

The cable connecting the thermopile with a high sensitivity galvanometer should be well shielded within a metal tube and if high frequency oscillations of considerable power are in operation in the building it is well to connect across the cable, where it is attached to the couple terminals, a high frequency choke in order that, if the cable picks up high frequency pulses they will not run through the couple, there developing temperature differences through the Peltier effect.

The deflections of the galvanometer connected to the pile are at most small and it has become customary to amplify them to as much as 200 or more times. In as much as all mechanical disturbance in the galvanometer as well as transient electrical and magnetic effects picked up by the thermopile circuit are also amplified it is evident that high amplification is only justified if all extraneous sources of disturbance have been very strictly prevented. Mechanical disturbances which cause movements in the galvanometer coils may be eliminated quite completely by various shock absorbing devices. Air currents about the coils are not entirely prevented as galvanometers are usually housed but can be eliminated by enclosing the instrument in a vacuum case or even an air-tight one if temperature differences can be avoided.

When all outside disturbances have been eliminated there still remain the Brownian movement effects of the galvanometer coil and similar effects of an electrical nature in the thermocouple circuits which cannot be eliminated. From this it appears that currents from the thermopile which cause galvanometer deflections of the same order of magnitude as the Brownian movement effects cannot be amplified to advantage. These effects

set a definite limit to the minuteness of the infra-red energy which may be measured by these methods. For the circuit employed in the spectrograph of Fig. 2 the r.m.s. deflection of the light beam at the camera drum due to Brownian movement of the galvanometer connected to the thermocouple is about 4 mm. When the deflection is 400 mm the mean error in the deflection will be about 1 percent.

There are a number of well-known amplifiers used to increase deflections. For recording instruments it is very important that there be no drift. As the instrument of Fig. 2 is a recording instrument the amplifier which amplifies 200 or more times is a periodic one,[7] that is it amplifies only impulses applied to it of a definite period. By operating a shutter at the entrance slit at this same period, 16 sec., only the galvanometer deflections arising from the thermopile currents are amplified, and drifts are quite completely eliminated. The advantages from amplification do not lie in larger deflections simply. They permit the use of the more stable D'Arsonval type of galvanometer which is quite free from magnetic disturbances.

Both types of spectrographs shown in Figs. 1 and 2 require very accurately made cones and calibrated circles otherwise the errors in determining the position of the grating may result in larger errors of measurement than would arise from all of the other sources of variation.

Infra-red observations by telescope and scale or by other similar devices for reading galvanometer deflections by eye are very tedious operations and for some time recording methods have been making their appearance. A good recorder usually reduces very materially the actual time required to measure a given spectral region. Moreover the accuracy with which lines may be measured are not unfavorably affected. Direct comparison of measurements of the rotational lines of water vapor over an appreciable spectral range made by a manual spectrometer and by a recording one showed an average deviation in values of 0.035 cm^{-1} with a maximum deviation of 0.07 cm^{-1}. The measurements were not only made at different times by different observers but upon different spectrographs with different gratings. With the recording instrument just mentioned weaker lines are

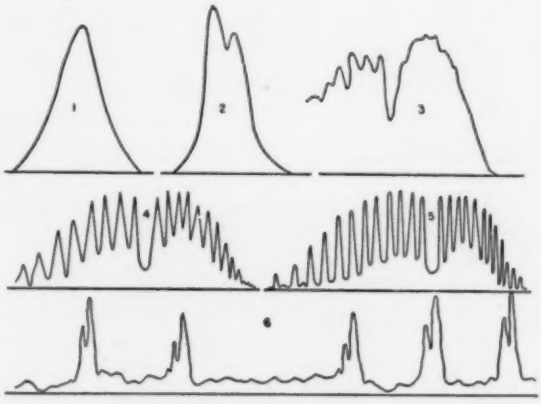

FIG. 6. The band of HCL at 3.5μ. 1, Angstrom and Palmer, 1893, width of slits 4000A. 2, Burmeister, 1914, slits 400A. 3, von Bahr, 1914, slits 100A. 4, Brinsmade and Kemble, 1917, slits 70A. 5, Randall and Imes, 1919, slits 39A. 6, Meyer and Levin, 1929, slits 7.5A.

regularly recorded that would usually be passed over in manual observation. Not only is the actual time in covering a given spectral region less but it may be possible to make the recording so automatic that, having once been started, no further attention will be required, the operator returning later at his convenience, the mechanism having automatically stopped the record upon its conclusion. This saving of time is an important factor and is often sufficient to permit the operator to measure entirely one record while a second one is being made. In Fig. 4 is recorded the rotational spectrum of D_2O between 31μ and 38μ.[8] While this particular record was run in the slowest time of operation, namely, eight hours, it is evident that no drifts have adversely affected this recording. Usually sufficiently satisfactory records may be obtained in much shorter periods, namely a little over two hours. In this case, if one record was being measured while another was recording, the fifty lines between 31 and 38μ would be completely measured in less than three hours.

The record of Fig. 4 is one giving energy distribution only and if one wished percentages of absorption in addition to wave-lengths it would have been necessary to run on this same record immediately before or after this record was made, a second record with no absorbing vapor in the optical path. The time required for this together with the measurements necessary to obtain percentages of absorption would be about

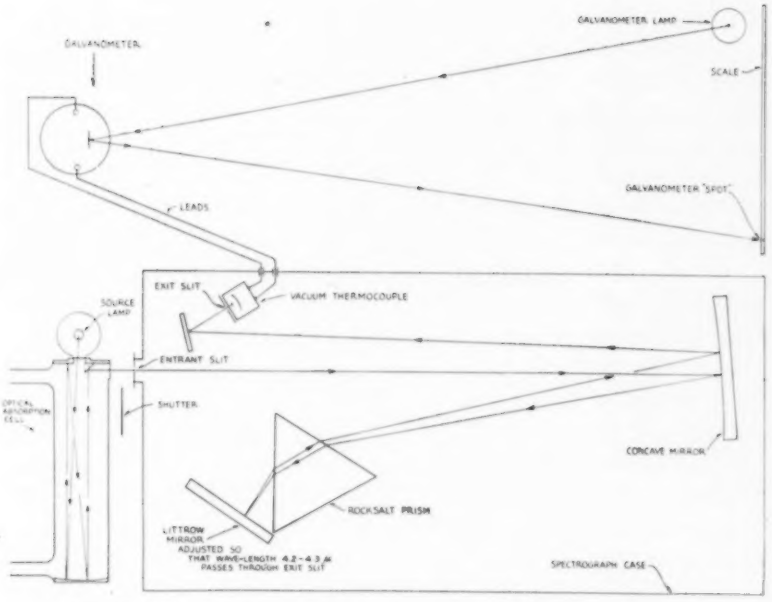

FIG. 7. McAllister recording spectrograph used in investigations in photosynthesis.

the same as the time required for the wavelength measurements alone. Several instruments[9] which record the percentages of transmission directly in the near infra-red have recently appeared. They are in fact spectrophotometers. Fig. 5 shows the record made by one of these instruments and was recorded in 35 minutes. It is quite certain that recording spectrographs will generally replace the manual instruments. In addition to saving the worker much time and tedious observation there is a very real advantage from having the original records preserved for future use or comparison.

The problem of molecular structure as it has developed has placed upon the experimental physicist the necessity of continually improving his spectroscopic equipment. While Fig. 2 represents a modern spectrograph for the far infra-red, Fig. 1 is a simple first arrangement. It embodies the essential ideas but has been superseded by instruments featuring many improvements. Ever higher resolution has been required. Fig. 6 represents what higher resolution makes possible in developing the fine structure in the HCl band system. A similar development has occurred in the case of the H_2O molecule at 6μ where in the latest work sharp absorption lines as close as 0.35 cm^{-1} have been sufficiently resolved for measurement.

In the far infra-red an investigation of the rotational spectrum of water vapor shows a similar improvement. The region is near 100μ. In 1924 the grating used had 25.4 lines per inch with a total of 71 lines. In 1939 the grating had 360 lines per inch and a total of 7200 lines. In 1924 the effective slit width was 10 cm^{-1}, in 1937 it was 0.22 cm^{-1}. As a result of this higher sensitivity and correspondingly greater resolution, the rotation spectrum of heavy water,[8] D_2O, has recently been measured with the result that some 210 absorption lines have been measured with an average uncertainty in their frequencies of around 0.03 cm^{-1}. It speaks well for the advance in theoretical physics that the majority of these lines have been accounted for, some 110 distinct rotational energy levels being determined.

As the difficulty of obtaining atoms of sufficiently simple structure and open spectra for satisfactory analysis increases, infra-red investigators are turning more and more to the field of organic chemistry where a purely empirical development of great significance is taking place, some results of which have been tabulated in Table I. These results which are generally well established, need to be greatly extended and the shifts in the measured frequencies under varying conditions observed and interpreted. Illustrations of a few of the generalizations to emerge from these studies will give an idea of their nature. When a compound, YOH, is dissolved in a solvent X there appears in the infra-red absorption spectrum in addition to the line of normal frequency for OH at 3300 cm^{-1} a second broader line of somewhat smaller frequency which has been interpreted to mean that a part of the YOH molecules form weak compounds with solvent molecules, X, through the establishment of a hydrogen bond. The amount of such association

is indicated by the intensity of the displaced OH line.

If several of these compounds Y_1OH, Y_2OH, Y_3OH, etc. are arranged in order of their solubilities, it is found[10] that the shifts of the new lines due to the hydrogen bonds when the Y hydroxides are dissolved in the solvent X are of different magnitudes, the order being the same as that of the solubilities. Reversing this relation it will be evident that where the greatest shifts occur upon association there will be the largest solubilities.

It appears also that the magnitude of the shifts, $\Delta\nu$, which occur when the OH bond is involved in a loose inter- or intramolecular bond can be used as a measure of the energy of such a bond. Badger has proposed the empirical relation:

$$\Delta\nu/\nu \propto D,$$

where D is the energy of the bond.

When the absorption spectra of complex materials of biological importance such as leaves, vegetable and animal tissue, plant pigments, etc. show infra-red absorption lines characteristic of C−H, N−H, O−H, etc. they do not add much to what is known of these materials since chemical studies have already shown the presence of compounds containing these groups. The occurrence of shifts in these lines to lower frequencies might indicate however that some of the complex materials were held together through the formation of hydrogen bonds.

An organic reaction is often accompanied by a minor reaction, a product of which constitutes an impurity in the main product. The presence of such an impurity may be detected and the quantity estimated provided this impurity alone possesses some one of those groups which give rise to an absorption line. While in general such materials can be detected and measured by purely chemical methods the infra method, if applicable, may be very much faster, and in some

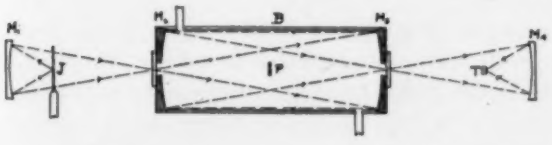

FIG. 8. Apparatus for the measurement of the absorption of gases and vapors in the air by the Pfund method.

kinds of operation this is a very important factor particularly in industrial operations. X-rays have now an established position in many industrial laboratories. The installation of an adequate x-ray equipment would mean that the

FIG. 9. Evaporograph of furfural ($C_4H_3O\cdot CHO$) between 4μ and 9μ by Czerny method.

x-ray physicist could immediately begin to carry out many well developed tests, and establish lines of research with a certainty of obtaining the results anticipated. It must be admitted that infra-red spectroscopy stands at the threshold only of such a development. It is noticeable, however, that those industries which have established infra-red research laboratories have not discontinued them but rather have amplified them with the passage of time. To date they are found mainly in the oil, gas, and rubber industries.

Infra-red absorption spectra may be obtained without altering, or dissociating the materials under examination, as might occur if ultraviolet light were used. The materials may be in the solid, liquid or vapor phase. X-rays require the materials examined to be crystalline and even then will not locate the hydrogen atoms. The Raman spectra of bonds involved in association seem to be extremely weak and diffuse and require very long exposures while with infra-red the measurements may be nearly instantaneous. Electron diffraction methods require the materials to be in vapor form, which limits their applicability.

In considering the possibilities of infra-red spectroscopy in dealing with complex organic molecules it should not be forgotten that these molecules are not simply aggregates of the groups contained in Table I but are unit structures which have characteristic frequencies. With molecules

of the great complexity of many organic compounds, distortional vibrations may occur of very low frequencies which will lie in the far infra-red. The isomeric forms of such compounds could not be distinguished from each other by the frequencies of Table I since the same groups are present in all the isomers. The shifts in the frequencies of these group lines as the groups took different positions within the molecule would be small and, with a number of isomeric forms present, would be masked. In the far infra-red, however, the frequencies due to distortional vibrations might differ appreciably with the location of the shifting groups. This spectral region appears to offer distinct promise if proper dispersion and resolution are used.

The uses of infra-red spectroscopy most in evidence at this time have already been presented at some length; namely, to obtain data from which the molecular structure of simple molecules may be deduced theoretically, and to study empirically the spectra of the complex organic compounds, tying up as far as possible the chemical properties of a material with its spectrum. There are many other uses some of which may be cited as typical. The absorption of CO_2 gas in long cells at high pressures gave new bands from which it was possible not only to amplify the theory of the structure of this molecule but also to identify bands observed on the planet Venus as due to CO_2, thus finding it possible to add materially to our knowledge of that planet's atmosphere.[11] The results indicate for example that the quantity of CO_2 in this planet's atmosphere is at least one hundred times that found in the earth's atmosphere, while the minimum temperature at the base of the layer is of the magnitude $t > 50°C$.

Applied to other planetary atmospheres certain bands of methane (CH_4) and ammonia (NH_3) have been found on Jupiter, Saturn, Uranus, and Neptune. Employing the sun as source and the atmosphere as absorption cell, the continuous absorption by water vapor has been determined between 8 and 14μ, and the discrete absorptions have been mapped and identified. The problem of the transmission of the atmosphere as a function of atmospheric water vapor is nearing completion. A new atmoshperic layer, comparable to the ozone layer in extent, and believed to be composed of oxides of nitrogen, has been found. And a graybody temperature of 7000°K has been determined for the sun in the spectral region 8μ to 14μ.

In the field of biology a striking improvement in the method of following the carbon dioxide assimilation and respiration of living plants, which is practically instantaneous, has resulted from developing a spectral absorption method[12] for determining the CO_2 contents of the air. This method is exceptionally sensitive and at the same time remarkably rapid. Through its use in studies of photosynthesis a number of very significant discoveries have been made. The method is equally well adopted to studies of any type of respiration: human, animal, or tissue cultures. It has obviously many uses in quite other fields, including that of industry. Fig. 7 represents the scheme of the apparatus with the absorption cell at the lower left hand. This recording spectrograph is a very excellent example of an infra-red prism spectrometer where the double use of a 60° prism has given the instrument a very good dispersion. Where high resolution is not required such instruments are most advantageously used. Nearly all of the present observations on complex organic molecules are done with prism spectrographs, many of them using the prism but once.

A still more recent[13] method for measuring the amounts of certain gases and vapors found in air, makes use of the infra-red molecular emission and absorption of the gases in question. The method is very sensitive and requires no spectrographic resolution of the infra-red radiation. The scheme of the apparatus employed is shown in Fig. 8, where J represents a jet of the gas to be measured heated to a high temperature, the characteristic radiations from which proceed through the absorption cell B and are focused through a suitable window upon a small receiving chamber T. This chamber, filled with this same gas, absorbs this characteristic radiation with a corresponding rise of temperature which is detected and measured by a couple within the chamber. When air containing this gas is passed through B, the selective radiation is partially cut off from the thermopile receiver with a fall in temperature of the couple which depends upon

the amount of gas present. No such effect is observed however if this gas is not in the air passed through *B*. When the gas will not permit heating without decomposition, a solid radiator may be used at *J*.

A study of the radiation heat from the human body has resulted in the measurement of the emission, reflection, and transmission of infra-red radiation by the human skin. This research[14] in the field of biophysics possesses significance since this information has direct bearing upon the heat-regulating mechanism of the body. Among the results established is that the human skin emits essentially as a blackbody radiator, and that for infra-red radiations negro and white skins reflect about the same.

These illustrations are typical of many that might be presented to show the uses of infra-red spectroscopy in allied fields of science. Carried on as they have been in close collaboration with workers in the other field involved, they represent one of the most promising developments of the present time, where each of the sciences concerned in a problem in a mid-field is capably represented by its specialist. A biologist attempting to solve his problems by the use of highly developed physical equipment or a physicist attempting to enter the biological field, work by comparison under great handicaps. This the industries have long recognized.

Possibly a good way to close a paper which has dwelt perhaps too exclusively with experimental methods, would be to describe a relatively new and very promising method of registering infra-red spectra which, if it succeeds, will render obsolete much of the beautiful infra-red equipment now in use. This method[15] covers one side of a thin film of Celluloid with a suitable absorbing medium; upon the other side a thin layer of a special oil is evaporated. The film and oil together are thin enough to give bright interference colors when suitably illuminated. When a spectrum is projected upon the blackened side, there will be evaporation of the oil from the warmer to the cooler areas. This action is rapid if the film is in a space saturated with the vapor of the oil. The changing thickness of the oil with evaporation will result in a change in the interference colors and the pattern thus produced may be photographed. Fig. 9 shows the infra-red absorption spectrum of furfural in the neighborhood of 5μ. Lines 0.1 mm apart on the photographic plate may be separated. Spectra to 10μ have been recorded.

Bibliography

1. Dudley Williams and L. H. Rogers, J. Am. Chem. Soc. **59**, 1422 (1937).
2. W. W. Sleator, Astrophys. J. **48**, 125 (1918). H. M. Randall and E. Imes, Phys. Rev. **15**, 152 (1920).
3. H. M. Randall, Rev. Sci. Inst. **3**, 196 (1932).
4. R. W. Wood, *Physical Optics*, third revised edition (Macmillan, 1934), p. 227.
5. A. H. Pfund, J. Opt. Soc. Am. and Rev. Sci. Inst. **14**, 337 (1927). A. C. Hardy, Phys. Rev. **38**, 2162 (1931).
6. C. H. Cartwright, J. Strong *et al.*, *Procedures in Experimental Physics* (Prentice-Hall, 1938), p. 331.
7. F. A. Firestone, Rev. Sci. Inst. **3**, 163 (1932).
8. From the unpublished records of Nelson Fuson.
9. A. C. Hardy, Washington Meeting Am. Phys. Soc., 1939. Not yet published. H. Gershinowitz and E. Bright Wilson, Jr., J. Chem. Phys. **6**, 197 (1938).
10. W. Gordy, privately communicated.
11. Arthur Adel and V. M. Slipher, Phys. Rev. **46**, 902 (1934). Arthur Adel, numerous papers in Astrophys. J. from 1937 to 1939.
12. E. D. McAlister, Smithsonian Misc. Coll. **95**, 24 (1937); J. Gen. Physiology **22**, 613 (1939).
13. A. H. Pfund, privately communicated.
14. A. C. Hardy and Carl Muchenhein, J. Chem. Investigation **13**, 817 (1934).
15. M. Czerny, Zeits. f. Physik **53**, 1 (1929). M. Czerny and P. Mollet, Zeits. f. Physik **108**, 85 (1937); Zeits. f. tech. Physik **18**, 582 (1937).

Very complete bibliographies of all phases of infra-red spectroscopy are found in the following texts:

G. B. B. M. Sutherland, *Infra-red and Raman Spectra* (Methuen and Co., London, 1935).

C. L. Schaefer and F. Mattossi, *Das Ultrarote Spektrum* (Julius Springer, Berlin, 1930).

Ergebnisse der Exakten Naturwissenschaften, Vol. 17 (Julius Springer, Berlin, 1938).

1. "Fortschritte auf dem Gebiete der Ultrarottechnik," M. Czerny and H. Röder.
2. "Ergebnisse der Ultrarotforchung," F. Mattosi.

Molecular Emission Spectra

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I. Introduction

THE present article is to deal with molecular emission spectra, and this necessarily restricts it almost exclusively to the spectra of diatomic molecules. The reason for this is that if polyatomic molecules are brought into a discharge tube or an arc in order to obtain their emission spectrum they break up readily and what is usually observed are the spectra of simpler constituents. Very often diatomic radicals are thus observed which are ordinarily not stable. For instance, a condensed discharge through water vapor gives the spectrum of OH, NH_3 furnishes NH, any hydrocarbon gives CH and C_2. The latter is a type of molecule unknown to the chemist but easily observed in a discharge tube or an arc. Another example of this kind is He_2, the spectrum of which has been very thoroughly studied. In the discharge tube the helium atoms become excited and excited helium atoms do not retain the properties of a noble gas and therefore can form genuine molecules which live long enough to emit a very extensive spectrum. Besides these pathological molecules, one meets of course also all the familiar diatomic molecules, such as H_2, N_2, HCl, etc. The molecular spectra are emitted by the molecules in the gaseous state and accordingly one expects to be able to observe the spectra of all those diatomic substances which can be obtained in the gaseous state. Substances which dissociate at high temperatures before they vaporize, or which break up as soon as they are electrically excited, will not produce band spectra. An example of the latter type of molecule is NaCl, which exists as a gas at high temperatures, but does not have any excited electronic state in which it is stable. Such molecules will give only a continuous absorption spectrum. Among this class of molecules must also be counted the molecular ion of hydrogen H_2^+ which is of special interest as the simplest of all possible molecules, as it has only one electron besides the two nuclei.

Occasionally, in certain cases, a polyatomic molecule will give an emission spectrum. A good example is CO_2 which under the proper conditions emits a spectrum rich in lines. This spectrum has, however, the same structure as that of a diatomic molecule, because the CO_2 molecule is linear. There are a few other examples of emission spectra of polyatomic molecules, but they are usually weak and diffuse and nothing like a complete analysis can be accomplished.

If we restrict ourselves therefore in this article essentially to the spectra of diatomic molecules, we shall not omit anything of importance. Polyatomic molecules can be studied spectroscopically either by their absorption spectra or by their Raman spectra which are dealt with in other articles.

Molecular spectra are also called band spectra because of the band-like structures which are seen in most of them, especially under low dispersion (Fig. 1), whereas an atomic spectrum or line spectrum always shows a number of distinct lines. These band-like structures can usually be resolved, under high dispersion, into a large number of individual lines, but the names band spectrum and molecular spectrum are now used synonymously even in cases when the appearance of the spectrum does not show a trace of bands. An example of the latter type of spectrum is the molecular spectrum of hydrogen (Fig. 2) which shows only a great number of lines without a trace of a band-like structure and without any apparent regularities. Such a spectrum used to be called a many-lined spectrum, and in an extreme case might be mistaken for an atomic spectrum upon superficial examination. However, such cases are rare (they are possible only for the very light molecules) and ordinarily it is possible to tell at a glance whether a given spectrum is due to a molecule or to an atom.

II. Energy Levels of Diatomic Molecules

In order to see what can be learned from the analysis of a band spectrum we must first have an idea of the structure of a band and how it is connected with the structure of the molecule.

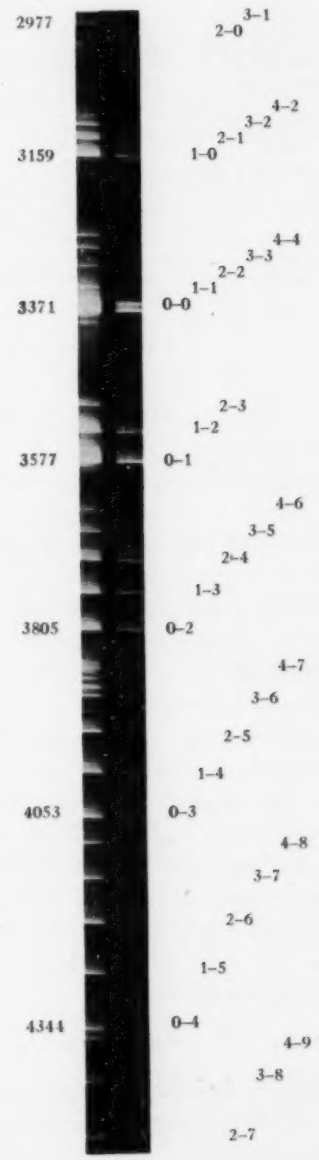

FIG. 1. The spectrum of a vacuum discharge in air. It consists chiefly of the second positive nitrogen bands which are produced by the neutral molecule of N_2. The vibrational analysis of the system is given at the right of the figure. The bands of this system have the appearance of typical bands with a sharp edge. They are degraded toward shorter wave-lengths. Under higher dispersion they are resolved into distinct lines. The NH band at 3350 is also prominent on the figure and faintly the OH band at 3064. The oxygen molecules contained in the air do not show up at all spectroscopically.

A molecule, like an atom, has a number of electrons which move in definite orbits. Ordinarily the electrons all occupy those orbits in which they have the lowest energy. If, however, the molecule is subjected to the bombardment of electrons or ions as it would be in a discharge tube or an electric arc, one of the electrons, usually the outer or most loosely bound one, is knocked out of its usual orbit and brought into an orbit with a higher energy. It can then return to any level of a lower energy and in doing so will emit the energy difference as light of the frequency ν according to:

$$h\nu = E' - E''.$$

So far we have not taken into account that the nuclei can also move; to this approximation each electronic transition would give one line just as in the atomic case.

However, the nuclei are not stationary in an actual molecule. They can perform two types of motion; they can vibrate along the line which joins them, and also the molecule as a whole can rotate about its center of gravity. Let us consider the oscillations first. The two atoms which form the molecule are held together by forces which are the valence forces of chemistry. For large distances they are attractive, while for very small distances they are repulsive forces. There is an equilibrium position for a certain separation r_e of the nuclei where the forces are zero. If we draw a diagram of the potential energy as function of the internuclear distance r (Fig. 3), then the force between the two atoms is given, for each internuclear distance, by the slope of the potential curve. For the equilibrium position r_e, the force is zero, which means that the tangent to the potential curve must be horizontal; the potential curve must therefore have a minimum at this point. The potential curves of diatomic molecules all have more or less the shape of Fig. 3. In the vicinity of the equilibrium position the force is harmonic; that is, the force is proportional to $r-r_e$, the departure from the equilibrium position. This means that the potential is proportional to $(r-r_e)^2$, and the potential curve is a parabola. But when we get farther away from the equilibrium position the situation changes. On the side of smaller distances it becomes in-

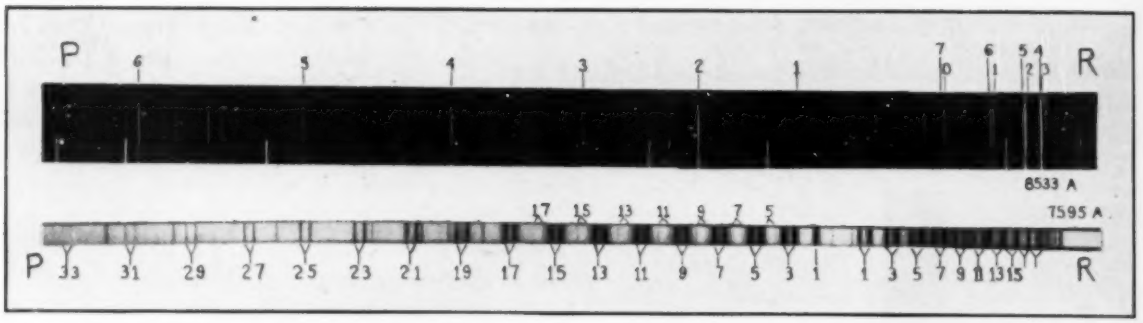

FIG. 2. Upper part. *A* band of D_2 with the head at 8533A. It is also of the simplest type, having only a *P* and *R* branch. Characteristic for the spectrum of the hydrogen molecule is the wide spacing of the lines and the small number of lines. The part reproduced contains about 300 angstrom units. This band is relatively free from lines belonging to other bands. In most parts of the spectrum so many bands fall in the same wave-length region that the regularities are completely obliterated and the band structure hidden. Lower part. The so-called *A* band of oxygen at 7595A which is taken by absorption through the earth's atmosphere. The lines are all double. The spacing is very much closer than for hydrogen although the scale is about 3 times that of the hydrogen spectrum. All the even numbered lines are missing. On the top of the spectrum are marked the lines belonging to $O^{16}-O^{18}$. The even numbered ones are not absent in this case but are invisible because they are hidden by the much stronger $O^{16}-O^{16}$ doublets.

creasingly more difficult to bring the atoms closer together, which means that the potential curve becomes steeper and must have a vertical asymptote for $r=0$, as an infinite force would be required to bring the nuclei completely together. On the side of greater distances the force becomes gradually smaller and for very large distances the mutual attraction of the two atoms is very small. For large values of r, therefore, the potential curve must come to a horizontal asymptote. The vertical distance between this asymptote and the horizontal tangent at the potential minimum (the equilibrium distance) represents the work necessary to separate the two atoms completely, starting from the equilibrium distance; in other words it is D_e, the work necessary to dissociate the molecule from the equilibrium position.

The molecule can perform vibrations about the equilibrium position. For small amplitudes they are harmonic vibrations and the energy is that of a harmonic oscillator

$$E_v=h\omega(V+\tfrac{1}{2}), \quad (V=0, 1, 2, \cdots)$$

where ω is the frequency of vibration and V an integral number, the so-called vibrational quantum number. For larger amplitudes the particular shape of the potential curve must be taken into account, but if the potential curve is known, the energy levels can always be calculated. In Fig. 3 these vibrational energy levels are indicated as horizontal lines. It is to be noted that the lowest level corresponding to $V=0$ is not $E_v=0$ which would be the energy of the molecule in the equilibrium position but $E=\frac{1}{2}h\omega$. In its lowest vibrational state the molecule has therefore half a quantum of vibrational energy which is called zero-point energy, because it persists even at absolute zero. The deviations from the harmonic binding shown by the actual potential curve have the consequence that the vibrational levels instead of being equidistant will come closer and closer together.

Besides performing oscillations the molecule can also rotate as a whole. If the internuclear distance in the equilibrium position is r_e, and $\mu=m_1\cdot m_2/(m_1+m_2)$ is the reduced mass, then $I_e=\mu r_e^2$ is the moment of inertia for rotation around the center of gravity about an axis perpendicular to the internuclear axis. It is well known that the rotational energy under these conditions has the values

$$E_r=(h^2/8\pi^2I_e)K(K+1), \qquad (1)$$

where K, the rotational quantum number, is also an integer. $Kh/2\pi$ is the angular momentum of the rotation.

In a molecule the three kinds of motion occur simultaneously, which means that the total energy is the sum of electronic, vibrational and rotational energies:

$$E=E_e+E_v+E_r.$$

In writing down this expression for the total energy we have not taken into account any kind

of interaction between the three kinds of motion. E.g., when the molecule vibrates the internuclear distance and therefore the moment of inertia change all the time. In the expression for the rotational energy we must then take some kind of an average value of the moment of inertia. The rotation will also affect the vibration, as the centrifugal force produced by the rotation will have to be subtracted from the binding force. The rotation and vibration may also distort the electronic motion. The effect of these interactions on the energy is relatively small except in extreme cases.

Frequently the interaction between vibration and rotation on the one hand and electronic motion on the other hand is practically negligible. The energy can then be expressed in the following way,

$$E=E_e+hc\sum_{l,\,m}Y_{lm}(V+\tfrac{1}{2})^l K^m(K+1)^m. \quad (2)$$

E_e is then a constant (the electronic energy) independent of the rotational and vibrational quantum numbers K and V. The second term of the right side is the energy of the rotating oscillator, that is of a model in which two particles are bound together by a potential of the type represented in Fig. 3, and which can be expressed in the vicinity of the equilibrium position by

$$V=hca_0s^2(1+a_1s+a_2s^2+\cdots);\qquad s=(r-r_e)/r_e. \quad (3)$$

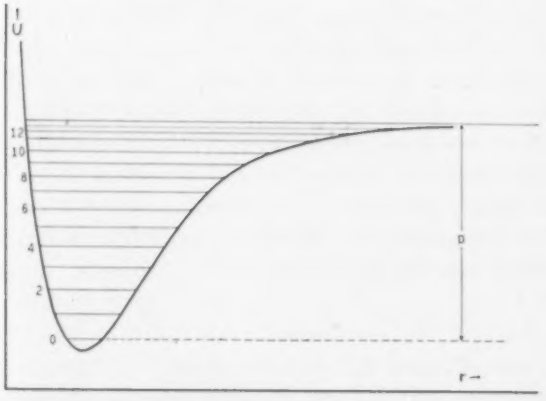

FIG. 3. The potential curve for the normal state of the hydrogen molecule. It is typical for many others, but for heavier molecules the vibrational levels are closer together.

The constants Y_{lm} occurring in the expression for the energy can then be expressed approximately in terms of the coefficients a_i in the potential energy as follows: with $\omega=2(Ba_0)^{\frac{1}{2}}$ and $B=h/8\pi^2c\mu r_e^2$

$$\begin{aligned}
&Y_{10}=\omega=2(Ba_0)^{\frac{1}{2}},\\
&Y_{20}=(3B/2)(a_2-5a_1^2/4),\\
&Y_{30}=\frac{B^2}{2\omega}\Big(10a_4-35a_1a_3-\frac{17}{2}a_2^2+\frac{225}{4}a_1^2a_2-\frac{705a_1^4}{32}\Big),\\
&Y_{01}=B=h/8\pi^2c\mu r_e^2,\\
&Y_{02}=-4B^2/\omega^2,\\
&Y_{03}=(16B^3/\omega^4)(3+a_1),\\
&Y_{11}=(6B^2/\omega)(1+a_1),\\
&Y_{21}=\frac{6B^3}{\omega^2}(5+10a_1-3a_2+5a_3-13a_1a_2+7.5(a_1^2+a_1^3),\\
&Y_{12}=-\frac{12B^4}{\omega^3}(9.5+9a_1+4.5a_1^2-4a_2).
\end{aligned} \quad (4)$$

The last three Y_{lm}, in which both indices are different from zero, express the interaction between rotation and vibration. The expression (2) for the energy is a good approximation only if the amplitudes of the vibration are small and also if the molecule does not rotate too fast, which conditions are met for relatively small values of V and K. What the limiting values are cannot be said in general. For H_2, for which the situation is particularly unfavorable as, due to the lightness of the molecule, large vibrational amplitudes correspond to relatively small values of the vibrational quantum number, the expression (2) should not be used for values of V larger than 2 nor for values of K larger than about 8. For heavier molecules, however, values of V up to 20 and of K up to 100 and more may be permissible.

The question of what to do when the expression (2) breaks down has never been settled satisfactorily. Various other expressions for the potential energy have been proposed. They have

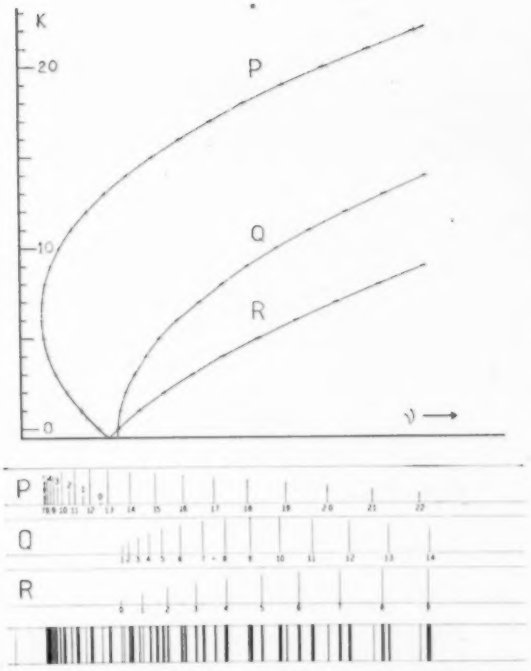

FIG. 4. Upper part: Fortrat diagram of a typical band. Below: The individual branches separately with their intensities. On the lowest diagram all three branches are drawn together as they would actually appear in a spectrum. It is seen that even for a band of this relatively simple type, the resultant structure may appear quite complex.

either the same limitations as (2) and (3) or are so complicated to handle that they are of comparatively little use. However, two of the methods deserve being mentioned. The first uses the Morse potential:

$$U=D(1-e^{-ax})^2.$$

It has the advantage over (3) that it gives for all values of the internuclear distance a curve which resembles in shape the true potential curve. Furthermore the vibrational energies of this potential are very simple, i.e.

$$E/hc=\omega(V+\tfrac{1}{2})-x(V+\tfrac{1}{2})^2$$

with

$$\omega=\frac{a}{2\pi c}\left(\frac{2D}{\mu}\right)^{\frac{1}{2}},\quad x=\frac{hc\omega}{4D}.$$

However, this formula cannot, because of its too great simplicity, give good quantitative agreement, and unfortunately it is not of the type which can easily be generalized.

The second method is of a more practical nature. If the actual potential is given, e.g. in the form of a curve, then it is always possible to find the actual vibrational energies by numerical or graphical methods; conversely if the energies are known empirically a potential curve can be constructed with fair accuracy. The chief disadvantage of this method is that it becomes too cumbersome if any precision at all is required, except when elaborate calculating machines are available.

In general one must be satisfied with the expression (2). From the band lines actually observed it is possible, when the data are sufficiently complete, to find an expression for the vibrational and rotational energy of each electronic state. In this case, the Y_{lm} values are empirically given. With the help of (4) it is then possible to find the constants for the potential curve. In general only a_0, a_1 and a_2 can be relied on to have any accuracy, but in favorable cases and for molecules that are not too light, one can go further. The internuclear distance can, in general, be obtained with great precision from the relation $Y_{01}=B=h/8\pi^2c\mu r_e^2$.

III. Structure of Band Spectra

Although all emission spectra of diatomic molecules are produced in analogous ways, namely by a simultaneous change in rotational, vibrational and electronic energy, the appearance of the band spectra of different molecules can be entirely different and we shall now examine the causes for this, and try to understand some of the details in the structure of the band spectra.

a. Rotational Structure

The electronic energy differences are, in general, much larger than the vibrational energy differences and these latter are, in turn, much larger than the rotational energy differences. All the lines produced by all the possible different rotational transitions but for one fixed vibrational and electronic transition will therefore lie close together. Such a group of lines is called a band. The frequency of all the lines in one band is given approximately by

$$\nu=\nu_0+B'K'(K'+1)-B''K''(K''+1),$$

where K' and K'' are the rotational quantum numbers of initial and final state and $B=h^2/8\pi^2I$. As the electron which produces the electronic transition participates in the binding of the

molecule it is natural that the binding force and internuclear distance are different when this electron is in different orbits. That is the reason why we have two different values of B, that is B' and B'', in the above expression. Now it is well known that the quantum number K, which represents the angular momentum of the molecule, can only change by ± 1 or 0. We have therefore the three possibilities

$$\begin{aligned} &K'-K''=+1, \\ &R(K)=\nu_0+2B'(K+1)+(B'-B'')K(K+1), \\ &K'-K''=-1, \\ &\qquad P(K)=\nu_0-2B'K+(B'-B'')K(K+1), \quad (5) \\ &K'-K''=0, \\ &\qquad\qquad Q(K)=\nu_0+(B'-B'')K(K+1), \end{aligned}$$

where ν_0 is called the origin of the band. The names P, Q, and R branch are quite universally used for these three cases, respectively. Very frequently the Q branch is absent; in other cases there may be only a Q branch and no P and R branches.

The structure of a typical band is represented in Fig. 4. The upper part gives the representation of the frequencies of the lines as a function of the rotational quantum number. Such a diagram is called a Fortrat diagram. The curves are parabolas, as is seen from (5). Below is found a representation of the branches as they would actually appear in the spectrum but with the three branches separated, and finally the complete band is given as it is actually observed. The Eqs. (5) and Fig. 4 show the chief characteristics of a band. The distance between successive lines in the P and R branches is approximately $2B$ in the immediate vicinity of the origin. This means that light molecules have their lines widely separated whereas heavy molecules have them close together. The range of B values which actually occur is from 60 cm^{-1} for the normal state of H_2 to about 0.03 for a heavy molecule like I_2. In the latter case it is usually very difficult to resolve the lines of a band even with the largest spectrographs, due to the fact that small separation of the lines is always accompanied by a large number of lines in each branch.

The figure also shows the formation of the head. Due to the quadratic term in (5) the lines in the P branch come closer and closer together with increasing K. For $K+\frac{1}{2}=B'/(B'-B'')$ the distance between two successive lines has become zero and the lines will proceed from then on to the opposite side. That means that for the integer value of K closest to this we have an edge usually called the head. If, as in Fig. 4, $B'-B''$ is positive, the head is in the P branch and the band is said to be degraded toward the violet; if $B'-B''$ is negative the head is in the R branch and the band is said to be degraded toward the red. Both kinds of bands occur with about the same frequency. If $B'-B''$ is negligible, then there is no marked convergence of the lines and the band does not have a head at all. An example of this type of band is the strong NH-band at 3350A (visible on Fig. 1). In extreme cases, as for example in the ultraviolet bands of O_2, the internuclear distance may change so much that the head is in the vicinity of the first line of the branch. As the first lines are usually weak, this type of band also does not have a pronounced head.

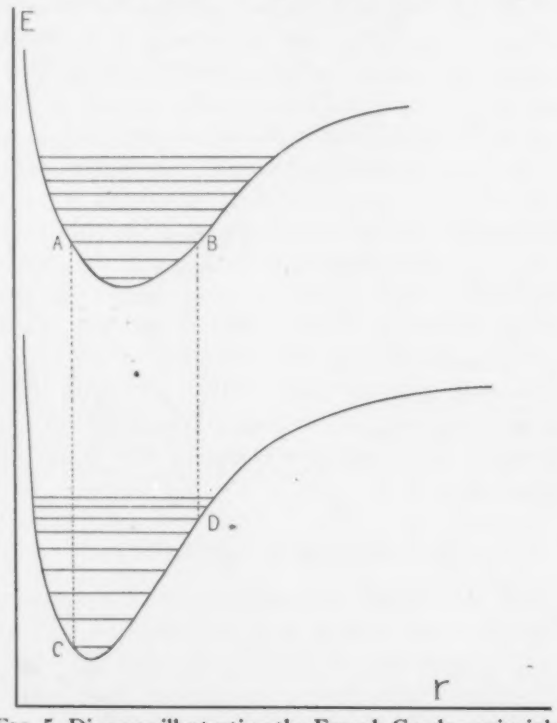

FIG. 5. Diagram illustrating the Franck-Condon principle.

The derivation of the properties of bands has been made under the assumption that there is no interaction between the different types of motion. If the various interactions are taken into account,

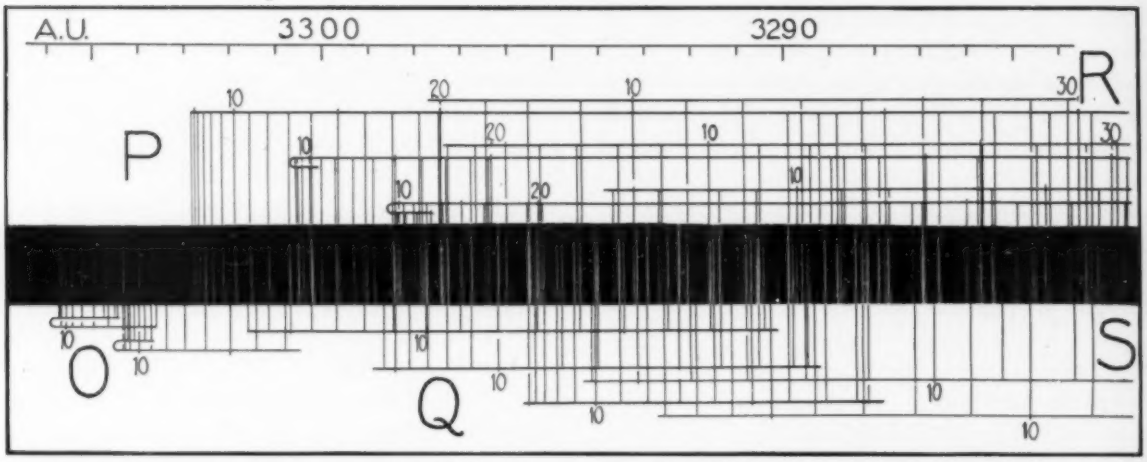

FIG. 6. Part of the 0→3 band of the so-called third positive group of CO. The figure shows the great complexity which the bands may have, if the interaction with the electronic spin plays an important part.

modification in the structure of the bands results. The interaction between rotation and vibration which was expressed in the energies by the formulae (2) and (4) introduces only small quantitative changes but leaves the general appearance of the band unchanged. However, the fact that the electron has a spin produces, just as in atomic spectra, a multiplicity of the lines. The fact that the magnetic field produced by the rotation of the molecule can act on the spin may produce quite complicated changes in the structure of the band, which, however, lie outside the scope of the present paper. These and other interactions are, however, perfectly understood. They may produce bands with many more than three branches. For instance all the bands of the so-called third positive group of CO have 27 branches (Fig. 7).

b. Vibrational Structure

All the bands belonging to one electronic transition are alike in structure and are said to form a band system. They differ only by their vibrational transitions. Leaving out the usually relatively unimportant higher terms the vibrational energy is

$$E_0=h\omega(V+\tfrac{1}{2})-x(V+\tfrac{1}{2})^2$$

and therefore the origins of a given band system are represented by

$$\nu_e+\omega'(V'+\tfrac{1}{2})-x'(V'+\tfrac{1}{2})^2 -[\omega''(V''+\tfrac{1}{2})-x''(V''+\tfrac{1}{2})^2].$$

This is the formula (somewhat modified) which Deslandres found for the heads in a band system long before there was any theory of molecular spectra. Now we use this formula for the *origins* of the bands as they have a definite physical meaning, namely the line into which the band would contract if there were no rotation. However, the same formula will hold with only slight modifications for the *heads* of the bands.

The selection rule for the vibrational quantum number V is not that of the infra-red bands where the bands with $\Delta V=1$ are by far the strongest. The selection rule and intensities of the bands can be calculated if the properties of both electronic states are known. However, these calculations are in general rather involved and therefore a method first proposed by Franck and then further elaborated by Condon, which allows us to obtain a qualitative picture of the intensity distribution, is very useful. It is called the Franck-Condon principle and rests on the fact that the motion of the electrons, because of their smaller mass, is much faster than that of the nuclei. Assume that the electron is in an excited state and that the molecule is in a certain vibrational state, e.g. $V=2$. (Fig. 5.) While the molecule oscillates, the nuclei pass the equilibrium position with great velocity and will spend only a very short time in that vicinity. However, at the two extremes A and B they move very slowly and are therefore most likely to be found there at any arbitrary moment, e.g. at the moment when the electron makes the transition from the upper state to the

lower state. This transition occurs in a very short time and therefore the nuclear distance cannot change appreciably during that time. In Fig. 5 that transition is therefore represented by the vertical line AC or BD.

Let us consider the point D. The molecule is left with a considerable amount of potential energy, as the distance is considerably different from the equilibrium distance for the lower electronic state. It will therefore vibrate with an energy which corresponds to the horizontal going through D, which will be in our particular case at $V=6$. It is immediately obvious that if the upper and lower electronic states had had very similar potential curves there would have been no change in the vibrational energy. The more the two curves are different, and in particular, the more the equilibrium distance r_e changes in the electronic transition, the larger will be the change in the vibrational quantum number. The transition from the point A will leave the molecule in the $V''=0$ state.

The model from which the Franck-Condon principle is derived is a little oversimplified, as the electron transition can also take place when the nuclei are not in their extreme positions, although with less probability. Also we know that the quantum-mechanical treatment will introduce some modifications. But we know as well that in all such cases the results derived from a simple classical model combined with sound physical judgment will be approximatively correct. This means that in our case we do not expect that the bands arrived at in the above way of reasoning are the only ones which can exist, but we do expect that they will be the strongest ones and that the neighboring transitions may also occur but with gradually diminishing strength. The farther away a transition is from the transition indicated in the figure by the vertical lines, the weaker it will be in general.

The Franck-Condon principle explains completely most of the peculiar differences in the structure of the various band systems. The emission spectrum is usually produced by the molecule in its normal state being bombarded by electrons which induces one of the outer electrons of the molecule to go to an excited orbit. For this excitation by electronic impact the Franck-Condon principle obviously applies, just as well as for the transitions by radiation, because the electronic impact can do very little to change directly the internuclear distance. Unless the temperatures are very high by far the greatest number of molecules will be in the lowest vibrational state. If the upper and lower states have the same equilibrium distance, electronic impact will produce excited molecules which are also preponderately in the $V'=0$ vibration state, and they will emit only the $0\rightarrow 0$ band. Under these conditions we see that we obtain a band system consisting chiefly of the $0\rightarrow 0$ band, with the $1\rightarrow 1$ band the next strongest. Such a system is the band of NH which was mentioned before as having the same internuclear distance in the upper and lower electronic state. On the other hand if the internuclear distance changes much, as for instance in the ultraviolet bands of O_2, the fourth positive group of CO, or the so-called $B\rightarrow A$ bands of H_2, we must expect both in absorption and emission large differences of the vibrational quantum number. We obtain then band systems with a large number of bands, sometimes more than a hundred. It may be that in such a system the $0\rightarrow 0$ band is so weak that it cannot be found at all. In such a case it may be quite difficult to decide what the vibrational quantum numbers really are. We shall come back to this point when we discuss the application of isotopic substitutions. The reader will have no difficulty in deciding for himself what the intensity distribution should be in intermediate cases.

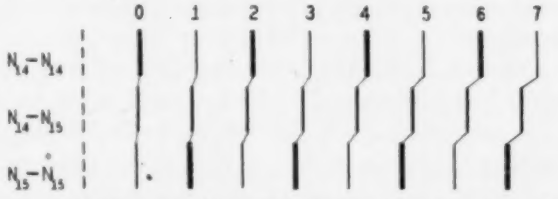

FIG. 7a. Diagram of an R branch for the three isotopic molecules of nitrogen. The origin of the band has been taken the same for all three cases. Observe also the alternating intensities for $N^{14}-N^{14}$ and $N^{15}-N^{15}$.

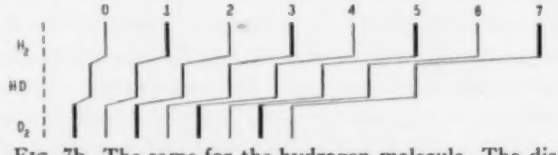

FIG. 7b. The same for the hydrogen molecule. The displacements are much larger than for N_2. (The scale is much smaller than in Fig. 7a.)

So much knowledge of the general structure of band spectra is necessary to understand any of the more specialized problems to which we shall turn our attention now. Of course there are very many interesting points, such as the influence of the electronic angular momentum and the electronic spin on the structure of the bands, which have played a great role in the development of the theory of band spectra and which produce such a variety of bands with different structures. However, I believe that this is of less general interest now than some of the other problems.

IV. Applications

After a band spectrum is photographed, measured, and analyzed, the question is then what information can be obtained from it concerning the structure of the molecule. The first and most direct result of the analysis of a band spectrum is the knowledge of the energy levels of the molecule which include rotational, vibrational, and electronic levels. From the preceding discussion it is apparant that the internuclear distance, the force constant, and more generally, the potential curve for the binding of the molecule, can then be obtained.

The heat of dissociation, because of its great practical importance, will be dealt with in a separate section. A knowledge of the above constants enables one to calculate thermochemical data such, as for instance, the specific heat, the entropy, and the heat content as functions of the temperature. The agreement with the directly observed (chemical) values is excellent but in general the band spectroscopic values are more accurate than the observed results. For diatomic molecules the situation is, in general, rather simple, and there are usually only slight deviations from the behavior predicted by classical statistical mechanics. On the other hand, for polyatomic molecules where the situation is more complex, the method of calculating specific heats, entropies and heat contents from band spectroscopic data often leads to results which could not have been obtained any other way. But even in simple cases new things come out occasionally. For example there was for a time very poor agreement between the observed specific heat of H_2 and that calculated from band spectroscopic data. This difficulty then led Dennison to the very important discovery of ortho- and parahydrogen.

a. Isotopes

The motion of electrons about a fixed charge is entirely governed by the magnitude of that charge. Therefore the energy levels in *atoms* are the same for different isotopes of the same element. Minute differences are usually due either to the fact that the nucleus is not entirely at rest (appreciable only in the hydrogen atom and the ions with one electron) or because isotopic nuclei differ also in other respects besides their mass. For example they usually have entirely different nuclear spins which produce a different hyperfine structure of the levels.

If the nuclei of diatomic molecules were fixed, the motion and energies of the electrons would also be the same for the molecules in which one or both of the constituent atoms have been replaced by their isotopes. However, the nuclei vibrate and rotate, and the rotational and vibrational frequencies and energies depend very markedly on the mass of the nuclei.

For harmonic vibrations the frequency is given by $\omega=(1/2\pi)(a_0/\mu)^{\frac{1}{2}}$ where a_0 is the force constant and μ the reduced mass. The vibrational energies which are $(V+\frac{1}{2})h\omega$ are therefore proportional to $1/\sqrt{\mu}$. Thus in order to obtain the vibrational frequency ω_2 of the isotope with the mass μ_2, if that of the isotope with the mass μ_1 is known, we have to multiply ω_1 by $(\mu_1/\mu_2)^{\frac{1}{2}}$:

$$\omega_2=\omega_1(\mu_1/\mu_2)^{\frac{1}{2}}=\rho\omega_1.$$

$\rho=(\mu_1/\mu_2)^{\frac{1}{2}}$ is called the isotopic factor, and all the other constants of the rotational and vibrational energy are converted from one isotope to the other by multiplying them by some power of ρ. For example, the rotational energy in first approximation is:

$$E_r=\frac{h^2}{8\pi^2\mu r_0^2}K(K+1)=BK(K+1)$$

and we see that

$$B_2=\rho^2B_1.$$

In general it can easily be shown that the constants $Y_{l,m}$ in the formula (2) are converted

by the $(l+2m)$th power of ρ, i.e.

$$Y_{2lm} = \rho^{(l+2m)} Y_{1lm}.$$

It should be added that these relations are not absolutely rigorous. The deviations are noticeable, however, only for the very lightest molecules and moreover the corrections can be calculated if the structure of the molecule is sufficiently known.

We can therefore say without restrictions that if the energy levels of a diatomic molecule are known, those of any isotope of this molecule can be derived from them. This has been checked experimentally in many cases. However, although the verification of the theoretical formulae for the isotopic shifts, which is at the same time a verification of the general theory of band spectra, may seem very gratifying, the importance of the isotopes for the study of molecular structure and band spectra goes much further.

But first we shall see what band spectra have done for the discovery of some of the isotopes. The work of Aston, Dempster and others with the mass spectrograph had established the existence of a large number of isotopes. There were, however, some elements, among them some of the most common ones, such as O, N, C, H, which seemed to be definitely single. However, there were in the atmospheric absorption bands of oxygen very weak lines for which no explanation had ever been found until Giauque and Johnston showed in 1927 that they could be explained completely by the existence of an oxygen isotope of mass 18. Aston immediately protested against this, saying that if such an isotope were present even to the extent of only one part in 500 he would have discovered it. To this Babcock replied that from the relative intensities of the $O^{16}-O^{16}$ and $O^{16}-O^{18}$ lines he estimated O^{18} to be present in a concentration of about 1 : 1250. This immediately showed the value of the band spectroscopic method in cases where only very small amounts of one of the isotopes were present. After attention was called to this fact by the discovery of O^{18}, a third isotope O^{17} of oxygen was found, and a search for rare isotopes of other of the common elements was made, with the result that soon after (Naudé, 1930) N^{15} was discovered from the absorption spectrum of NO, and C^{13} from the C_2 spectrum (King and Birge, 1930). Soon after this the heavy isotope deuterium of hydrogen was discovered by Urey, which has proved to be of such great importance for chemistry and physics.

It should be mentioned that some of the earlier estimates of the abundance ratios were considerably wrong, as the intensity measurements in band spectra, from which these ratios are determined, are very difficult, especially when the differences in intensities which have to be measured are so big. The mass spectrograph has been improved in the meantime, so that it gives reliable values of the ratios even if one of the isotopes is many hundred times more abundant than the other. The following table gives the abundance ratios of H, C, N, and O from later determinations.

$H^1 : D^2$	5000 : 1
$C^{12} : C^{13}$	92 : 1
$N^{14} : N^{15}$	265 : 1
$O^{16} : O^{18} : O^{17}$	503 to 640 : 1 : 0.2.

These are the abundances in the elements as they occur naturally and the data are from band spectroscopic intensities, mass spectrographic determinations or atomic weights. The various determinations agree fairly well for H, C, and N but the determinations of the $O^{16} : O^{18}$ ratio varies from 503 to 630, without it being possible to see which of the results should be preferred. It has been suggested that possibly the abundance ratio depends on the preparation of the sample and that therefore different observers may actually have had different abundances. The band spectroscopical value 640 of Mecke and Childs was obtained with ordinary atmospheric oxygen and if correctly measured should therefore represent the abundance ratio in the atmosphere.

Now let us see how the isotopes can help the band spectroscopist. One very vexing problem has always been the identity of the molecule which emits a particular band spectrum. The question is sometimes difficult, because some substances are so much more sensitive spectroscopically than others that they will produce a strong spectrum even if they are present in the light source only in very small amounts as impurities. If there is an isotopic molecule, however,

the isotopic shift will be different for each kind of molecule and this will identify the molecule which emits the spectrum. For example, the copper arc emits a series of bands of which it was very uncertain whether they were emitted by CuO, CuH, CuN or perhaps even Cu_2. Copper has two isotopes with atomic weights 63 and 65, and therefore all bands should be double. Actually the observed shift was extremely small, which showed immediately that the bands are due to CuH. For in that case the center of gravity is practically at the Cu-atom and this therefore contributes very little to the moment of inertia; so that it matters very little whether there is a Cu^{63} or a Cu^{65} atom. The small observed shift agreed exactly with this. Much later, when there was no longer any doubt about the identity of the molecule, the corresponding CuD bands were also found. In many other similar cases the identity of the emitting molecule could be established beyond any doubt. The fact that the separation of the isotopes has been possible for some of the most important atoms and therefore the rarer isotopes can be obtained pure, or at least in large concentrations, will make this method of identification of the molecule increasingly useful.

Another problem in the analysis of a band spectrum is very often the assignment of vibrational quantum numbers. If there is, for instance, a sequence of bands of which we know that they all have the same final state $V''=0$, then we know that the band with the smallest frequency must be the $0\rightarrow 0$ band and the following ones of larger frequencies $1\rightarrow 0$, $2\rightarrow 0$, etc. There can be no doubt about this if the $0\rightarrow 0$ band and those near it are of great intensity. (Compare Fig. 1 which shows such a case.) If, however, the intensity distribution is such that the bands gradually fade out towards longer wave-lengths, then we do not know whether the band with the lowest frequency is the $0\rightarrow 0$ band or whether there are other bands of the progression with even lower frequencies which have, however, such low intensities that they cannot be observed. However, if there is an isotopic molecule available, the doubt is immediately removed. For we know that the electronic frequency remains unchanged and that the vibrational energies change by the factor ρ. The observed shift tells us actually how much vibrational energy there is; in other words it gives us the value of the vibrational quantum number. Many examples are to be found in the literature where the analysis of difficult band systems was made easier in this way by the help of isotopes. The method is perhaps even more valuable for the analysis of the spectra of polyatomic molecules. It is obvious that without a correct assignment of the vibrational quantum number no reliable calculation of the molecular constants can be made.

We do not have to restrict ourselves to the vibrational structure to be benefited by the isotopic spectra. Whenever there is a doubt about any point in the analysis of a molecular spectrum, it can usually be cleared up if the analogous parts in the spectrum of an isotopic molecule can be studied.

Figure 8 gives as an example parts of the spectrum of N_2^+. The upper figure gives the $0\rightarrow 0$ band of ordinary nitrogen and shows clearly the R branch extending to the right and the P branch extending to the left, coming to a head and then going to the right. All lines are narrow doublets and the doubling can be clearly seen for high enough values of the rotational quantum number. This band is of the simplest possible type ($\Sigma\rightarrow\Sigma$). The reason that the lines are alternately strong and weak is taken up later on.

Figure 7a gives a diagram of the R branch where, however, the separation of the lines has been held constant. Below this are given the same lines for $N^{14}-N^{15}$ and $N^{15}-N^{15}$, their position calculated from the known isotopic factor. Fig. 8 shows that the actual lines behave in exactly the same way. The middle spectrum is taken with a concentration of about 30 percent and shows both $N^{14}-N^{14}$ and $N^{14}-N^{15}$ with about the same intensity. Finally the lower spectrum gives $N^{14}-N^{15}$ and $N^{15}-N^{15}$ with approximately equal intensities, which corresponds to a concentration of about 70 percent N^{15}. There is a small constant displacement to the left in addition in Fig. 8, which is due to the vibrational effect. Because of the half-quantum of zero point vibrational energy, there is a small difference of vibrational energy involved in the $0\rightarrow 0$ band which is different for the three isotopes. However, the fact that this vibrational shift is so small tells us immediately

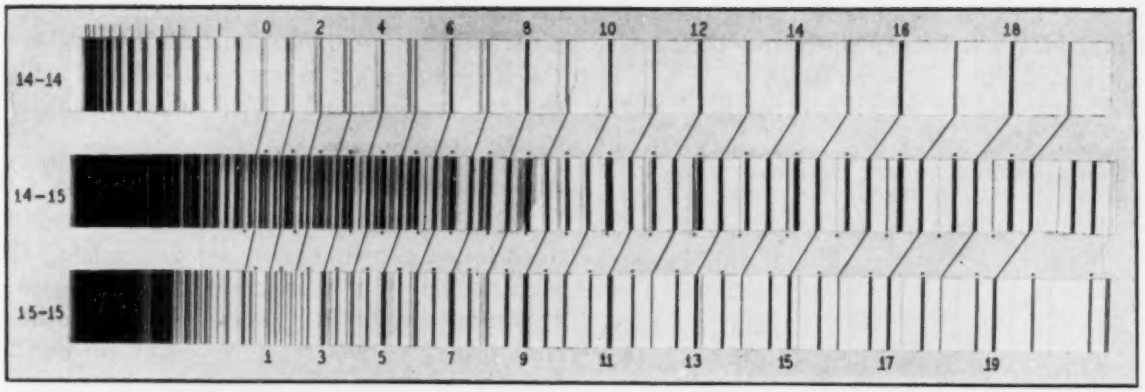

FIG. 8. The O→O band at 3914A of the negative nitrogen bands (N_2^+). (Wood and Dieke.) The upper spectrum is that of ordinary nitrogen $N^{14}-N^{14}$. The lines of the *R* branch are marked and the alternating intensities are seen. The strong lines are numbered (even *K*). The beginning of the *P* branch is also indicated. These lines get very soon too crowded and come to a head. The middle spectrum is taken with a concentration of about 30 percent of the heavy isotope N^{15}. The lines of the *R* branch of $N^{14}-N^{15}$ are marked. Those of $N^{14}-N^{14}$ are indicated by a dot above, those of $N^{15}-N^{15}$ by a dot below the line. It is seen that there are no intensity alternations for $N^{14}-N^{15}$. (Perhaps better seen on the lower spectrum where the lines are not overexposed.) The lower spectrum is taken with about 70 percent of N^{15}. The $N^{14}-N^{15}$ and the $N^{15}-N^{15}$ lines have about the same intensity, but the $N^{14}-N^{14}$ are only faintly visible. The intensity alternations of the $N^{15}-N^{15}$ lines are now of such a nature that the odd numbered lines are the strong ones.

that we are dealing with the 0→0 band and not some other vibrational transition.

Figure 7b shows the diagram for the equivalent thing in H_2. As the mass of deuterium is twice that of hydrogen, the isotopic changes are much larger, in fact so large that there is very little apparent similarity between the spectra of H_2 and D_2.

The isotope shift has also been used to determine the relative masses of the isotopes. For, as we saw before, all the molecular constants of one isotope are found by multiplying those of the other one by certain powers of the isotopic factor ρ. If these constants are determined empirically for both isotopes, the value of $\rho=(\mu_2/\mu_1)^{\frac{1}{2}}$ is found and therefore the ratio of the reduced masses. However, in many cases some of the corrections to be applied are uncertain and with the improvement of the mass spectrograph, the latter instrument is in general probably capable of a more reliable determination of masses.

b. Heats of Dissociation

The energy necessary to separate a molecule completely into the two constituent atoms is usually called the heat of dissociation and is a constant of the molecule which is of great importance to physicists and chemists.

One way to determine the heat of dissociation is to subject the gas to such high temperatures that the thermal energy will dissociate a considerable percentage of the molecules. The larger the heat of dissociation, the smaller the percentage of the gas which is dissociated at a given temperature. Therefore by a measurement of the dissociation equilibria it is possible to determine the heat of dissociation. Unfortunately for many of the most common molecules the heat of dissociation is so large that at the temperatures which are experimentally feasible, only a negligible amount of the substance is dissociated. It is unfortunate that for most of the fundamental simple molecules any other way of determining the heat of dissociation thermochemically also leads to difficulties, so that we must rely for these important quantities almost entirely on the values obtained from molecular spectra.

The chemical heats of reaction allow a good determination of differences of dissociation energies, so that if some of the heats of dissociation of the fundamental molecules have been determined from band spectroscopic data, a number of others can be determined chemically.

There are several independent methods by which the heat of dissociation can be determined from the study of band spectra. The principle is the same in all of them, and they differ only in

the experimental details. Therefore first the general idea will be explained and then under *A*, *B*, etc. the individual methods.

Let us consider a normal potential curve (Fig. 3). The energy difference between the horizontal asymptote and the lowest vibrational

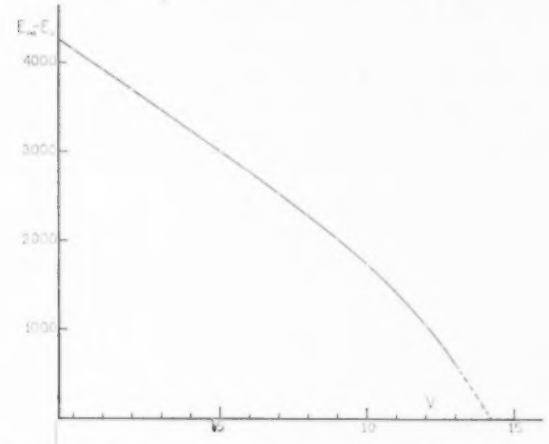

FIG. 9. $E_{V+1}-E_V$ as function of V for the normal state of H_2.

level ($V=0$) is the heat of dissociation. The spacing of successive vibrational levels becomes less with increasing vibrational quantum number. That this must be so with a shape of the potential curve as in Fig. 3 can be seen from the quantum condition

$$\oint p_r dr = \int (2\mu(E-U))^{\frac{1}{2}} dr = (V+\tfrac{1}{2})\cdot h,$$

which is the old Bohr condition for a stationary state and can be shown to be the first approximation in the more rigorous wave-mechanical treatment. Moreover the approximation is a very good one for a problem of the type we are dealing with. If the potential curve were a parabola, we would have an harmonic oscillator and the energy levels would be equally spaced. If, however, the curve is less steep on one side, the integral would give a larger contribution there for the same energy. To bring the integral back to its required value $(V+\frac{1}{2})\cdot h$ the energy will have to be lowered.

Above the limit of dissociation the energy can have any value, i.e. the distance between successive energy levels is zero. Below the dissociation iimit there are discrete levels, with the distance between successive levels therefore different from zero. The limit of dissociation is therefore the point where $E_{V+1}-E_V=0$ which can also be expressed $dE/dV=0$ with sufficient approximation.

A

This gives us a means to determine the heat of dissociation experimentally by determining the vibrational energy as function of the vibrational quantum number V. This can be done entirely empirically, without recourse to any theoretical formula expressing the relationship between E_V and V. We plot $\Delta E_V=E_{V+1}-E_V$ as function of V and extrapolate the curve until it intersects the V axis. Fig. 9 gives the example of the normal state of the hydrogen molecule where the energies are known up to $V=14$. The extrapolation is here very short. The sum of all the ordinates in the figure for integer V is the total energy at the point of dissociation, i.e. the required heat of dissociation. The value obtained in this way for H_2 is 4.454 volts or 102.70 kcal.

We see immediately that the accuracy of this method depends entirely on how reliably the extrapolation can be done, and this in turn is determined by what piece of the total curve is known empirically. If, as in the illustrated case, the known part of the curve reaches very close to the point where ΔE_V is zero, the accuracy is good. In many molecules, however, only a few vibrational levels are known and in those cases this method is of rather problematical value.

Just below dissociation the molecule vibrates with very large amplitudes and therefore the average moment of inertia I_V is quite large, i.e. the quantity

$$B_v=h/8\pi^2 c I_V$$

is small. At the point of dissociation the amplitude of the vibrations becomes infinite i.e. $B_V=0$. This fact also may be used to find the limit of dissociation. In Fig. 10 B_V is plotted as function of V for the same state to which Fig. 9 refers. We see that the extrapolation is short also in this case and that $B_v=0$ for about $V=15$.

From either Fig. 9 or Fig. 10 we see therefore that $V=15$ is the last vibrational state of the normal H_2 molecule which can possibly exist. It lies so close to the dissociation limit that even its existence is not completely certain.

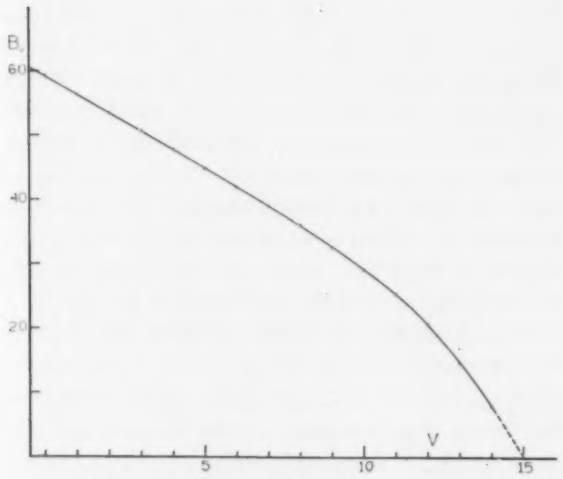

FIG. 10. B_V as function of V for the normal state of H_2.

B

The energy levels above the limit of dissociation are continuous, and transitions from them to another electronic state will produce a continuous spectrum at the short wave-length side of the discrete bands. Sometimes the long wave-length limit of this continuous spectrum can actually be observed accurately, and that furnishes an excellent method for the determination of the heat of dissociation. Usually the conditions for this are more favorable in an absorption spectrum. H_2 again furnishes an example for this.

There is a strong absorption spectrum of hydrogen in the extreme ultraviolet. From about 1100 to 850 it consists of sharp bands due to transitions from the normal state to two excited states ($2p\ ^1\Sigma$ and $2p\ ^1\Pi$ in Fig. 11). At 845.61A there is a sharp inset of the continuous absorption. Beutler found that this limit has a rotational structure, which is due to the fact that the molecules with all different degrees of rotational energy can absorb.

The absorption edge for the rotationless molecule lies at 844.77A which corresponds to an energy of 14.6029 volts. This is the energy necessary to bring the molecule into an excited state and dissociate this excited state. Obviously the two hydrogen atoms which result cannot be two normal atoms, for we know that the heat of dissociation cannot possibly be 14.6 volts. One of the resulting atoms must therefore be an excited atom. In this case we see easily that it must be an atom in a two-quantum state, for we have already an approximate value for the heat of dissociation. Also in this particular case an analysis of the molecular states of H_2 shows that the state in question must dissociate into a normal and a two-quantum atom. We must therefore subtract from the absorption limit the energy of excitation, which is very accurately known, and obtain

Absorption limit	14.6029 ev
Energy of excitation of atom	10.1476
Heat of dissociation	4.4553

This value agrees excellently with the one obtained by the first method.

In the case of the hydrogen molecule there is no doubt about the nature of the atomic states into which the molecule dissociates. In other molecules, where the data are not as complete and the state of affairs is more complicated, there may be uncertainty about the nature of the excited state of the atom. In such a case a wrong value of the heat of dissociation will result, and examples are known in the literature

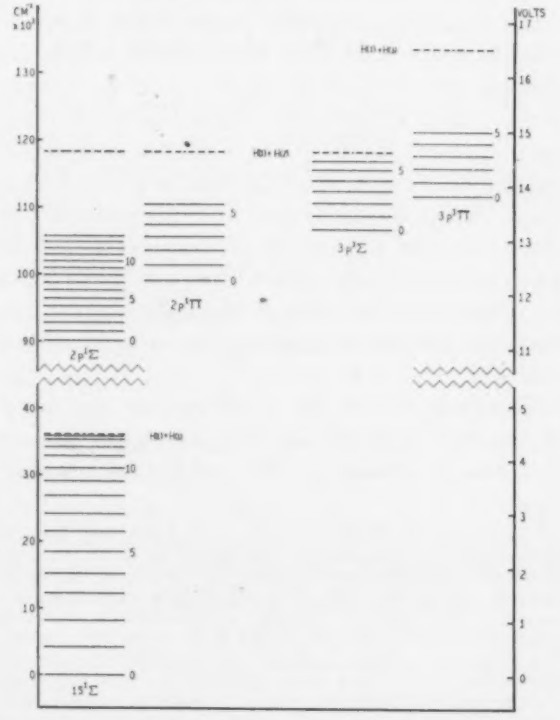

FIG. 11. The vibrational levels for several electronic states of H_2 and their dissociation limits.

when the error was several volts. (CO has been a particularly bad case.) Such an error is, of course, not due to errors in the measurement, but due to an erroneous interpretation which can always be avoided if the nature of the molecular states is sufficiently known.

The method A of extrapolating the vibrational differences, which was used for the normal state of hydrogen, can be used in exactly the same way for any of the excited states, provided we know what the state of excitation of the resulting atom is. For H_2 this yields values for the heat of dissociation which are in agreement with the two values already given, although the accuracy is less, as the extrapolation must be carried out over a larger range.

C

A third way of determining the heat of dissociation makes use of the phenomenon known as *predissociation*. A very instructive example for this is also found in the hydrogen molecule.

On the right side of Fig. 11 two electronic states* $3p\,^3\Sigma$ and $3p\,^3\Pi$ are shown with their vibrational structure. There are transitions from these two states to a common final state $2s\,^3\Sigma$ which give rise to some of the strongest bands in the H_2 spectrum. The $3p\,^3\Pi \rightarrow 2s\,^3\Sigma$ bands are the well-known Fulcher bands, and they consist of P, Q and R branches. These bands have the peculiarity that the Q branches are completely regular in all cases, whereas the P and R branches show many irregularities and are completely absent for the higher vibrational levels ($V>3$). The explanation for this is that the $3p\,^3\Pi$ state is really double. The two components are normally very close together for each rotational state.

The Q branches are produced by the lower of the two components and its properties are such that it cannot be affected by the presence of the $2p\,^3\Sigma$ state, while the upper doublet component which is responsible for the P and R branches interacts with the $2p\,^3\Sigma$ state. We do not need to go into the detailed mechanism of this kind of interaction, except that it occurs strongly only if two levels with the same value of the rotational quantum number K are close together. A characteristic feature of such interaction is that the molecule oscillates rapidly between the two different electronic states.

As long as the $3p\,^3\Pi$ level in question is below the dissociation limit of $3p\,^3\Sigma$ the chief visible effect of this interaction is the displacement of the levels which results in the displacement of the lines. Such perturbations are quite a characteristic phenomenon in many band spectra.

If, however, the $3p\,^3\Pi$ level lies *above* the dissociation limit of $3p\,^3\Sigma$, there is always a state of the latter exactly coincident with it with which it can interact, as we have a continuous distribution of energy levels above the dissociation limit. The result of the interaction in this case is that the oscillation of the molecule between the discrete $3p\,^3\Pi$ and the continuous $3p\,^3\Sigma$ state will destroy the former, as dissociation will occur if the molecule is in the $3p\,^3\Sigma$ state. The lines which we would expect normally from the $3p\,^3\Pi$ states cannot occur, therefore, as the molecule will be destroyed before it has time to emit these lines.

That is exactly what is observed, and Fig. 12 gives a comparison of this set of levels for H_2, HD and D_2. We know that as long as we observe P and R branches, we are below the dissociation limit, but if there are only Q branches we are above it. Therefore by selecting the highest complete level and the lowest one with only Q branches, we know that the dissociation limit must lie between them. In our case the limits are 4.43 and 4.52 volts.

The fact that we have the three isotopic molecules helps considerably, because the dissociation limit is the same for all three isotopes. (The heat of dissociation is however different for different isotopes, as the $V=0$ levels, from which the dissociation energies are counted, have different positions.) Therefore we can compare the limits for the three isotopic molecules and narrow the interval in which the dissociation limit must lie. In our particular case the interval

* The symbols $3p^3\Sigma$ etc., are used here only for the identification of the states. The letters Σ, Π, Δ are used extensively for the classification of electronic states of diatomic molecules, and their meaning is that the component of the electronic angular momentum (exclusive of spin) along the internuclear axis is 0, 1, 2, respectively. The symbols $2s$, $3p$ etc., give the quantum numbers of the valence electron. The number signifies the total quantum number and the letters s, p, d, $\cdots$ that the angular momentum of the electron is 0, 1, 2, respectively. However these latter symbols have this significance only if the nuclei of the molecule are close together.

is 0.09 volt. As the width of the interval is determined largely by accidental circumstances, it may easily happen that another set of states is found where the interval is much narrower.

The more familiar way of looking at predissociation is by drawing the potential curves of the two states and observing that they intersect (Fig. 13). The molecule in the $2p\,{}^3\Pi$ state can then go over to the other potential curve and if its energy is above the dissociation limit of the $2p\,{}^3\Sigma$ state, will dissociate. A qualitative picture of the probability with which such transition occurs can be obtained by considering the speed with which the nuclei pass the point of intersection. If this is large there will be little chance that in the very short time they are in the vicinity of the intersection point, they will be able to change over to the other potential curve. We expect therefore the greatest probability for predissociation when the nuclei pass this point slowly, that is if the vibrational levels are in the vicinity of the intersection point. However, other considerations are involved which can be taken account of only with an adequate quantum mechanical treatment of the problem.

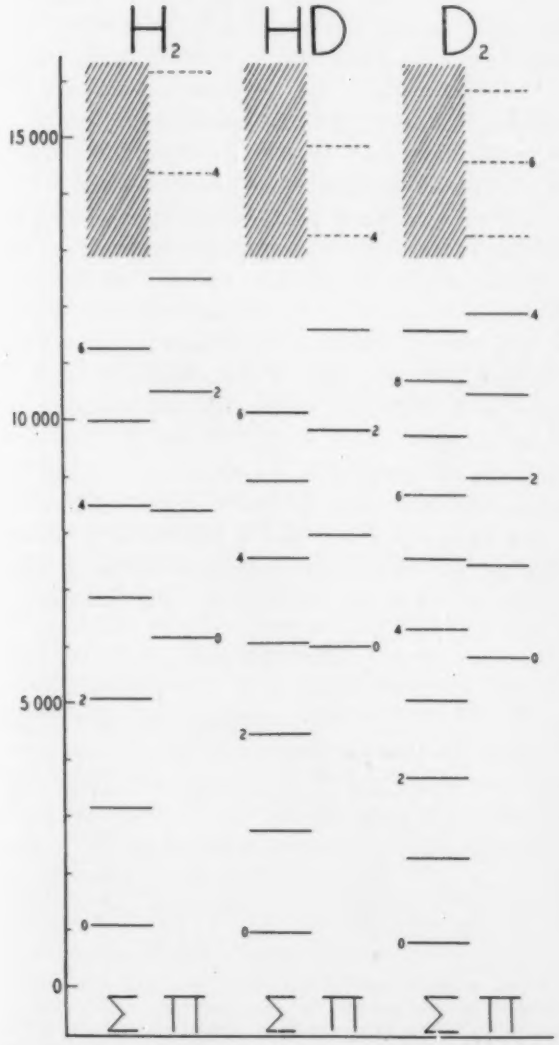

FIG. 12. The vibrational levels of two electronic states $3p\,{}^3\Sigma$ and $3p\,{}^3\Pi$ of H_2, HD and D_2. The levels shown by a broken line are predissociated.

D

The three methods for determining the heat of dissociation described so far are the most important ones and they can be applied to almost any molecule if the empirical data are complete enough. In some cases there are special conditions which make it possible to apply a method peculiar to those conditions. Let us illustrate this again with the hydrogen molecule.

If we start out with a normal hydrogen molecule we can dissociate it in the following two ways:

$$H_2 \xrightarrow{D} H+H$$

or

$$H_2 \xrightarrow{I} H_2^+ + e \xrightarrow{D^+} H+H^+ + e \xrightarrow{-I_a} H+H.$$

(The quantities written above the arrows are the energies required for the reaction.)

The total energy change in both cases must be the same which gives for the heat of dissociation D

$$D = I_m - I_a + D^+,$$

where I_m and I_a are the ionization potentials of the molecule and atom respectively and D^+ the dissociation energy of the molecular ion H_2^+. This quantity can be calculated theoretically with comparative ease as the H_2^+ ion contains only one electron and presents therefore a mathematical problem which can be solved much more easily than a similar problem for any other molecule. I_H, the ionization potential of the hydrogen atom, can be obtained with great precision from the atomic spectrum (it is the limit of the Lyman series and equal to the Rydberg constant). The ionization potential I_m of the molecule can be determined by electron impacts or spectroscopically as the limit of a

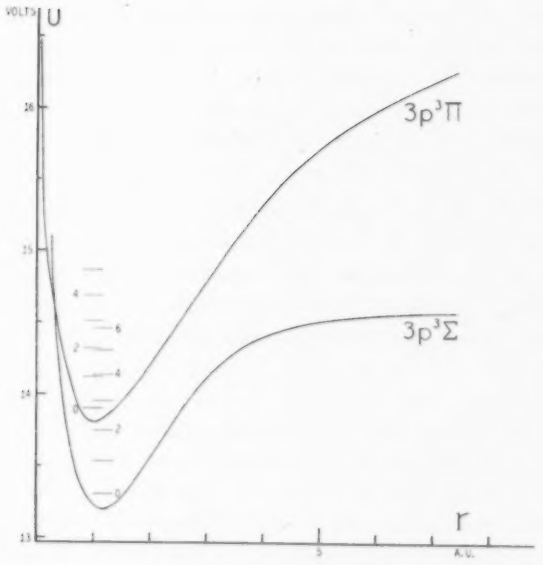

FIG. 13. The potential curves of the levels shown in Fig. 12.

Rydberg series. It is the quantity with the largest probable error and therefore the error of I_m is also the probable error of the heat of dissociation.

A similar procedure can be adopted in any case where for some reason the heat of dissociation of the ionized molecule can be found and at the same time the ionization potential of the neutral molecule.

Analogous relations can be used whenever the dissociation can be achieved in a circuitous way and the energies of all the intermediate processes can be either calculated or found experimentally.

Table I gives the results for some of the most common molecules. The values were obtained usually with one of the methods described, sometimes with several.

c. Determination of the Nuclear Spin

Most of the known nuclear spins have been determined either from the hyperfine structure of atomic spectra or from the intensity alternations in band spectra of symmetrical molecules. The hyperfine structure method is usually applicable only to rather heavy atoms, as only they show sufficiently large hyperfine structure separation. On the other hand the nuclear spin can be determined from band spectra only if the substance forms symmetrical molecules like H_2, O_2, He_2 etc. at least temporarily in a discharge tube. Furthermore it is necessary that the rotational structure can be resolved sufficiently so that intensity measurements of successive rotational lines can be made.

These conditions are fulfilled best for the light atoms and therefore the band spectra method has been most successful for some of the elements at the beginning of the periodic table.

The method is based on the Pauli exclusion principle, which states that any molecule or atom can exist only in states which have wave functions which are antisymmetric in the elementary particles.* An antisymmetric wave function changes its sign when two of the similar elementary particles are interchanged.

In order to see what influence the exclusion principle has on the structure of band spectra and how it is connected with the nuclear spin, we shall simplify the problem somewhat, retaining, however, all of the essential properties.

As we have seen above, the complete motion of a diatomic molecule can be considered to be composed of several parts. First the translatory motion of the center of gravity, which is of no importance for us so that we can assume the molecule to have no translatory motion. There remain then the motion of the electrons and the rotation and vibration of the nuclei. In accordance with this the wave function consists of three factors $\psi=\Phi\cdot$R.U., of which the first refers to the motion of the electrons, the second to the vibration and the third to the rotation.

We have to see now how ψ behaves if we interchange two elementary particles in the nuclei. However, the wave function is not a function of

TABLE I.

	VOLTS	KCAL./MOL.
H_2	4.455±0.001	102.72
N_2	7.34 ±0.02	169.2
O_2	5.09 ±0.03	117.3
S_2	4.45 ±0.01	102.6
CO	11.06	255.0
F_2	2.715	62.6
Cl_2	2.468	56.9
Br_2	1.962	45.24±0.07
I_2	1.535	35.40±0.03

* The explicit use of quantum mechanics has been avoided in this article, as the essential results can be understood quite well without it. For the treatment of the nuclear spin and the intensity alternations however, the use of wave mechanics is essential. Those unfamiliar with its use may turn directly to the third paragraph of page 798 and take the statements made there for granted.

the positions of the individual protons and neutrons of which the nuclei consist, but depends only on the position of the entire nuclei. We must therefore investigate how the wave function behaves if we interchange the nuclei. If the nucleus consists of A particles, i.e. has the atomic weight A, then the interchange of the two nuclei is equivalent to the exchange of A elementary particles. The exclusion principle demands that in each elementary exchange the sign of the wave function changes. This means that for the exchange of the complete nuclei the sign of the wave function changes if A is odd and remains unchanged if A is even. In other words, the wave function must be antisymmetric in the complete nuclei if the atomic weight is odd, and symmetric if it is even. This is sometimes expressed in the literature by saying that the nuclei satisfy Fermi-Dirac statistics for odd A and Bose-Einstein statistics for even A.

We have now to investigate the behavior of the wave functions under an exchange of the nuclei and exclude all those states which are not antisymmetric. To be definite we shall choose an atom with odd atomic weight for which therefore only antisymmetric states are allowed. Without any essential loss in generality we can assume that the electronic part of the wave function is *symmetric* in the nuclei. That is actually the case for the ground states of most molecules. Should an electronic state be antisymmetric instead, all the conclusions will be exactly reversed. The vibrational part of the wave functions is always *symmetric*, as it depends only on the internuclear distance r which is not affected by an exchange of the nuclei.

The behavior of ψ depends now on the behavior of the rotational part U of the wave function. We shall make the simplifying assumption that the molecule rotates about an axis fixed in space. Then the azimuth φ about this axis is the only coordinate on which the rotational wave function depends.

The wave equation in this case is

$$\frac{d^2U}{d\phi^2}=-\frac{h^2}{8\pi^2I}\phi,$$

of which the solution is

$$U=A\cos K\phi$$

with $K=0, 1, 2, \cdots$ the rotational quantum number, and A a constant.

If the nuclei are interchanged ϕ becomes $180°+\phi$ which makes U change sign for odd values of K and remain unchanged for even K. In other words the symmetry of the successive rotational states alternates.

If the rotational axis of the molecule is not fixed in space, the rotational wave functions will be spherical harmonics instead of the simple cosines. However, as can be easily checked, the alternating symmetry of the wave functions will not be affected.

The result so far obtained has not taken into account the existence of a nuclear spin and will therefore be true only for nuclei without a spin. If there is a nuclear spin of I units,* it will necessitate an additional factor in the wave function which will depend on the orientation of the two spins. We do not have to know the exact nature of the function and shall therefore merely call it

$$S(\sigma_1, \sigma_2),$$

where σ_1 and σ_2 can have all values from $-I$ to $+I$ in integer steps. If we interchange the nuclei the spin function becomes $S(\sigma_2, \sigma_1)$. It may be that

$$S(\sigma_1, \sigma_2)=S(\sigma_2, \sigma_1).$$

In that case S is symmetric. That is always the case if $\sigma_1=\sigma_2$. In general, however, the spin function will be neither symmetric nor antisymmetric. In that case we can introduce two new spin functions:

$$S_s=S(\sigma_1, \sigma_2)+S(\sigma_2, \sigma_1)$$

and

$$S_a=S(\sigma_1, \sigma_2)-S(\sigma_2, \sigma_1),$$

of which the first is symmetric and the second antisymmetric. That can be done for each state except when $\sigma_1=\sigma_2$ when only the symmetric functions exist.

We shall now ask how many symmetric and how many antisymmetric wave functions exist for a given nuclear spin I. There are $2I+1$ different values for σ_1 or σ_2 which means that there are $(2I+1)^2$ different combinations σ_1, σ_2. $S(\sigma_1, \sigma_2)$ and $S(\sigma_2, \sigma_1)$ have to be counted as two different states. Of these there are the $2I+1$

* This I has, of course, nothing to do with the moment of inertia which was also designated by I.

combinations with $\sigma_1=\sigma_2$ which produce only symmetric states and the remaining

$$(2I+1)^2-(2I+1)=2I(2I+1)$$

states are divided evenly between symmetric and antisymmetric spin states.

There are therefore $N_a=I(2I+1)$ antisymmetric states and

$$(2I+1)^2-N_a=(I+1)(2I+1)=N_s$$

symmetric states.

According to the exclusion principle the total wave function must be antisymmetric. We have therefore in our special case the possibilities

Orbital wave function		Spin wave function	Number of states
odd K	symmetrical	antisymmetrical	$I(2I+1)$
even K	antisymmetrical	symmetrical	$(I+1)(2I+1)$

For an electronic state of different type the situation would be just reversed, and likewise for nuclei of odd atomic weight. The important thing which is the same for any type of nucleus and any electronic state is that successive rotational states consist alternately of $I(2I+1)$ and $(I+1)(2I+1)$ states which are different only in the relative orientations of the nuclear spins. As the influence of the nuclear spin on the energy is negligible, these different states for the same K have all the same energy. Lines originating as transitions between these states consist therefore alternately of $I(2I+1)$ and $(I+1)(2I+1)$ coinciding lines, which means that the ratio of the intensities of successive rotational lines in one band is as $N_s/N_a=(I+1)/I$, everything else being equal. If the band of such a molecule is photographed this intensity ratio can be measured and from it the value of the nuclear moment found. In Table II the intensity ratio is listed for a number of values of the nuclear spin I together with the molecules for which this ratio was found. Examples of the intensity alternations can be found in Figs. 2 and 8. If there is no nuclear spin alternate lines are missing which can be noticed immediately. For small values of the nuclear spin only rough intensity measurements are required, as it is necessary only to distinguish between the widely different ratios 3 : 1, 2 : 1 etc. For larger values of the spin, the possibilities lie closer together, and more accurate intensity measurements are required, which are sometimes difficult to obtain. The method is therefore most useful for light molecules which have a moderate nuclear spin.

It is obvious that the method is only applicable when molecules with two identical atoms can be procured. Even if the two atoms are two different isotopes of the same element, the intensity alternations disappear completely. Obviously the method is of no use if the element cannot form diatomic molecules, as, e.g., beryllium or neon. However, it has been mentioned that several elements which ordinarily would not be expected to form molecules do so under suitable conditions, e.g., He_2, C_2, Na_2.

V. Calculation of the Energy Levels

Our knowledge of the detailed structure of diatomic molecules is practically all derived from the empirical data accumulated from the study of band spectra. In principle there is also another way which presupposes no experimental data whatsoever. For we know that a diatomic molecule consists of two nuclei with given charge and mass and a number of electrons. Furthermore we know the forces between all these particles, and in wave mechanics or quantum mechanics we have an instrument with which we can calculate then any desired property of the molecule. It is well known that in general mathematical difficulties prevent us from actually carrying out these calculations. For instance in most cases even a rough estimate of the positions of the electronic levels is difficult or impossible. Only for the very simplest molecules can we hope to get reasonably good results. Even in these cases the calculations are not easy and require often long and laborious numerical calculations.

The molecular ion of hydrogen, H_2^+, is the simplest of all possible molecules as it contains

TABLE II.

I	$N_s : N_a$	$\frac{I+1}{I}$	NUCLEI
0	1 : 0		He^4, C^{12}, O^{16}, S^{32}
$\frac{1}{2}$	3 : 1	3	H^1, F^{19}, K^{39}
1	2 : 1	2	D^2, N^{14}, ...
$1\frac{1}{2}$	5 : 3	1.67	Li^7, Na^{23}, K^{39}
2	3 : 2	1.5	
$2\frac{1}{2}$	7 : 5	1.4	Cl^{35}, I^{58}
∞	1 : 1	1	

only one electron besides the two nuclei. Accordingly its properties can be calculated with greater ease than for any other molecule. This has been done for the ground state by Hylleraas and for the excited states by Teller and others. Unfortunately there is little opportunity to compare the calculated results with observations as no spectrum of H_2^+ is known and the calculations show that it is very unlikely that one can be found, as practically all the excited states are so called repulsive states in which the molecule cannot exist. Empirical data for the lowest state, however, can be obtained by extrapolating the excited states of the neutral molecule to complete ionization. This was actually done by Richardson and a fair accuracy can be achieved. The results agree completely with the calculations. The importance of the H_2^+ calculations, however, does not lie in the fact that a few properties can be determined which can be compared with experimental data but in that here the calculations are rather straightforward and direct and some of the great difficulties met in other molecules (even neutral H_2) do not unduly complicate the problem. Therefore H_2^+ is an example which shows all the essential properties of a diatomic molecule which can be treated completely theoretically, and the behavior of more complicated molecules can often be found from this by analogy.

The same is true for the neutral H_2 molecule, although the calculations necessary to find theoretically the desired properties of the molecule are more complicated and require long and laborious numerical computations. However these calculations have been carried out successfully for a number of electronic states chiefly by James and Coolidge. The agreement with the experimental results is in general very good, and we have here the advantage over H_2^+ that for H_2 the empirical data are very complete. But again the purpose of these calculations is not to find theoretically a few energy levels. They can be obtained much more accurately from the band spectroscopic data, and that probably always will be so, even if the calculations can be carried out with a much higher accuracy than is possible at present. However to calculate other properties, besides the energy levels usually also the wave functions are required, and there is no simple way to obtain them from the spectra or any other experimental data. Therefore, one must rely for the knowledge of the complete wave functions entirely on these theoretical calculations. It may often be possible to use the same type of wave function approximately also for other, more complicated molecules. If the wave functions are known any property of the molecule can be found by simple integration.

The calculations of James and Coolidge are so far the only successful attempts to find complete wave-functions of diatomic molecules on which some reliance can be put. It is unfortunate that even in this simple case the wave functions are so complicated that their use is extremely difficult, but that seems to lie in the nature of the problem, and we have so far nothing else to take their place. For this reason the hydrogen molecule probably will always occupy a singular place among the molecules. It is fortunate that the spectrum of the hydrogen molecule contains a larger amount of significant empirical material than the known spectrum of any other molecule, so that there is ample opportunity to check all the results of the theoretical calculations and to guide them in the right direction.

Literature

It would probably serve no useful purpose to list here even a part of the hundreds of papers which have been written on band spectra and their applications to thermochemical problems. Therefore only a few papers and books of a general character are listed, in which more detailed information can be found and where detailed references to the literature are given.

1. R. S. Mulliken, "Interpretation of Band Spectra," Rev. Mod. Phys. **2**, 60 (1930); **4**, 3 (1932).
2. W. Weizel, "Bandenspektren," *Handbuch der Experimentalphysik*, Ergänzungsband (Leipzig, 1931).
3. W. Jevons, *Report on Band Spectra of Diatomic Molecules* (Cambridge University Press, 1932).
4. R. de L. Kronig, *Band Spectra and Molecular Structure* (Macmillan, New York, 1930).
5. H. Sponer, *Molekülspektren und ihre Anwendung auf chemische Probleme* (Springer, Berlin, 1936).
6. F. R. Bichowsky and F. D. Rossini, *The Thermochemistry of the Chemical Substances* (Reinhold, New York, 1936).
7. G. Herzberg, *Molecular Spectra and Molecular Structure* (Prentice-Hall, New York, 1939).
8. O. W. Richardson, *Molecular Hydrogen and Its Spectrum* (Yale University Press, 1934).

Astronomical Spectra
Modern Observation and Interpretation

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THE subject of astronomical spectra has grown enormously since that memorable occasion in 1802 when it occurred to W. H. Wollaston to substitute a narrow slit for the round hole used by Newton and his successors in the study of the solar spectrum.[1] Astronomical spectroscopy was born when Newton discovered the dispersion of sunlight by a prism, but it became a science when Wollaston found seven dark lines in the continuous spectrum. Since that time thousands of absorption lines have been discovered. The Mount Wilson revision of Rowland's "Preliminary Table of Solar Spectrum Wave Lengths," published in 1928, contains more than 20,000 lines. Thousands of new lines have since been measured, as photographic plates sensitive to longer and longer wave-lengths were produced. We possess at the present time fairly complete knowledge of the sun's spectrum from λ 2950A, where it is limited by strong atmospheric ozone bands, to λ 14μ, where the cut-off is caused by carbon dioxide.[2] An extension of the spectrum to λ 2000 might be possible at a height of at least 40 km. Saha[3] has seriously suggested the organization of a "stratosphere observatory," equipped with rockets or balloons which would carry small solar spectrographs to the required height. An extension of our knowledge of the sun's continuous spectrum in the ultraviolet region would be particularly valuable, because we strongly suspect a large excess of energy in the far ultraviolet. The stellar spectra are, of course, much less known, and nearly every month brings new lists of wave-lengths and identifications. Since the atomic spectra have been more or less completely analyzed by the physicists, the principal interest has, in recent years, passed to the molecular bands.[4] But only within the past six months the spectrum of Fe III has been analyzed by Swings and Edlén[5] and identified by them in the spectra of B-type stars.

It would be unprofitable to give an exhaustive description of all recent advances in astronomical spectroscopy. A volume could be devoted to the measurement and identification of absorption and emission lines and another volume to the interpretation of their intensities by means of the theory of ionization. I shall, therefore, describe in the following pages only a few of the highlights of modern astrophysics.

I. Spectra of Normal Stars

The spectrum of a normal star shows a continuous background with absorption lines on it. The great majority of spectra can be arranged, to a fair degree of approximation, in a one-dimensional array. This was done by Secchi, Vogel and others. The classification of stellar spectra now in use is that developed by Miss Annie J. Cannon at the Harvard Observatory. The principal physical parameter of this classification is the temperature.

When accurate methods are used for lining up the stars within the Harvard sequence it is found that there are a number of slightly conflicting criteria. For example, when we use the line λ 4045 of Fe I we may assign a star to a certain subdivision, corresponding to a temperature of 6000°, while when we use λ 4077 of Sr II we may feel inclined to place it among much hotter stars of, say, 8000°. These conflicting criteria show that the appearance of a stellar spectrum is not uniquely determined by the temperature. Some other parameter must be at work. This parameter is the pressure. Low pressure increases the ionization, as does high temperature. But the manner in which the temperature and the pressure affect the ionization is not the same. The equation of ionization,

first derived by Saha

$$\frac{N_2}{N_1}=\text{Constant}\times\frac{1}{P_e}\frac{T^{5/2}}{e^{\chi/kT}},$$

N_2 = No. of ionized atoms,

N_1 = No. of neutral atoms,

P_e = Pressure of electrons,

T = Temperature,

χ = Ionization potential,

shows that the ratio N_2/N_1, which measures the ionization, is inversely proportional to P_e, while it depends upon T in a complicated manner, depending upon the size of the ionization potential. Hence, elements having different ionization potentials are ionized differently in giants—where the pressures are low—and in dwarfs—where the pressures are high.

The spectral classification is, therefore, two-dimensional, the parameters being temperature and pressure. The question arises whether this two-dimensional scheme is exact, within the precision of present-day spectroscopic observations. The answer is that there still remain some small inconsistencies among the intensities of the various lines. These inconsistencies are not large enough to cause trouble when we are concerned with statistical investigations, but they promise to throw light upon additional physical parameters which affect the intensities of spectral lines. One such parameter has recently been discovered. It is designated as the turbulence of the stellar atmosphere. When the atmosphere is quiescent and the motions of the atoms within it are solely those of the Maxwellian temperature distribution the contour of an absorption line consists of a narrow Doppler core having a flat bottom and steep edges, and of wide wings the shape of which is determined by the effect of radiation damping. But when the Doppler effect is increased by macroscopic motions within the gas the central core becomes relatively more important. The lines appear broad and have steep edges. Only the very strong lines still display wings produced by radiation damping.

If we compare a star having large turbulence and one without turbulence we find that the faintest lines of both stars are of equal intensity if they belong in the same place of the two-dimensional classification. The intermediate lines of the turbulent star are much stronger than the corresponding lines of the quiescent star and, finally, the very strong lines should again be the same.

However, observation suggests that sometimes the strongest lines of the turbulent star are actually weaker than those of the quiescent star. This has not been definitely proved, but it seems that the phenomenon occurs only when the turbulent star is a supergiant. Evidently we are dealing with a new effect caused by pressure. Indeed, the phenomenon of collisional damping should be pronounced in the dense dwarfs, where it will produce wings of the same shape, but much more intense than those which are produced by radiation damping. In the supergiants the pressures are very low and collisional damping is absent. The wings are those of radiation damping.

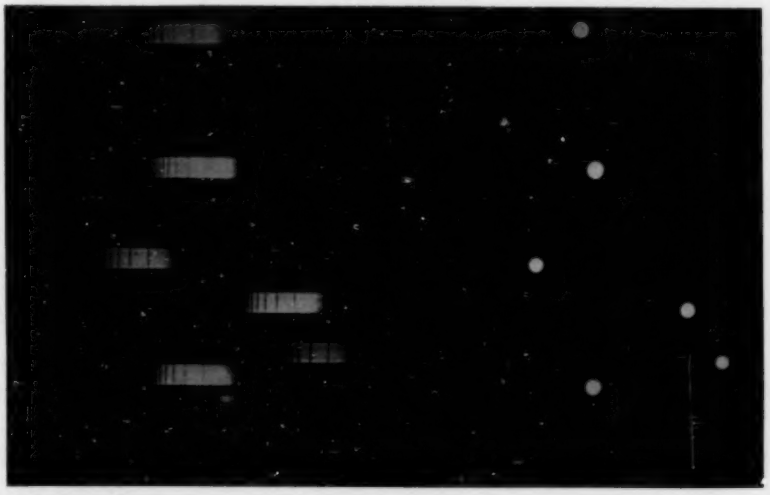

FIG. 1. On the right is an extrafocal photograph of the brightest stars of the cluster in the Pleaides. At the left is the same group obtained in focus with an objective prism in front of the lens. The images of the stars were permitted to trail for a short distance up and down in order to widen the spectra.

Another important phenomenon in the interpretation of stellar spectra is the ionic Stark effect which broadens the lines of hydrogen and those of neutral and ionized helium. This phenomenon is conspicuous when we compare the Balmer series in a giant (α Cygni) and in a dwarf (α Lyrae).

Finally, the observed contours of the lines are strongly influenced by the Doppler effect produced by the rotation of the star around its axis.

After allowance has been made for all known effects which influence the intensity and contour of a stellar absorption line there still remain some more or less conspicuous differences in the intensities. It is natural to attribute these effects to differences in the abundance of the various elements. It is possible, for example, that the division of the so-called Wolf-Rayet stars into a carbon sequence and an oxygen sequence, and the similar splitting of the spectral classification at the cool end may be due to excessive abundance of carbon and oxygen, respectively. But among the normal stars of intermediate spectral type the variations in abundance are very slight,[6] although in individual cases[7] the evidence seems to be rather strong that small departures in content are observable.

The origin of the stellar absorption lines has been thoroughly discussed by Unsöld.[8] If we are able to measure the total energy absorbed in a *faint* line we obtain a measure of the "equivalent width," usually expressed in equivalent angstrom units of complete absorption. This equivalent width

$$A_\lambda = \int k_\lambda d\lambda = \frac{\pi e^2 \lambda_0^2}{mc^2} NHf, \qquad (1)$$

where k_λ = absorption coefficient within the line for wave-length λ
e = charge of electron
m = mass of electron
c = velocity of light
N = number of atoms in the lower energy state of the line
H = height of absorbing layer
f = oscillator strength, measuring the probability that the transition in question will take place.

When f is known—and it can often be computed directly or inferred from analogy with the hydrogen spectrum—we can compute NH—the number of absorbing atoms in a column of one cm², in the line of sight. The expression does not depend upon the manner in which the radiation is transmitted through the gas, nor does it depend upon the form of the absorption coefficient. These simplifications are not present when the line is strong, for then not only its shape, but also its equivalent width depend upon the transfer of radiation and upon the form of the absorption coefficient. The quantity NH has a definite physical meaning if we can picture a stellar atmosphere as a mass of gas, reasonably transparent in all wave-lengths except in the line and overlying a definite photospheric layer where the continuous spectrum originates. Such a model may be used in many cases. For example, it should be close to the truth in stars surrounded by very large tenuous shells (ζ Tauri, φ Persei). But in normal stars the atmosphere is not transparent. The continuous absorption coefficient of the atmosphere, caused by such processes as photoelectric ionization of hydrogen and other elements, limits the depth to which we can see into the star's atmosphere, and the meaning of NH is not immediately obvious. Milne and others have discussed this matter in great detail and have shown how the absorption coefficient for continuous radiation and that for the line combine to produce the observed contour.

II. Anomalous Stellar Spectra

Among the few stellar spectra which fail to fit into the normal Harvard sequence is a group of hot stars which, in addition to absorption lines, show emission lines of hydrogen, ionized iron and of other elements. These spectra have been investigated by Merrill, McLaughlin and others. The emission lines are broad—ranging from one angstrom or less to ten angstroms or more. Usually the emission lines of hydrogen are superposed over a weak, broad absorption line, so that the outer wings produced by the Stark effect are visible flanking the emission lines. Hence, it is reasonable to suppose that we have a normal stellar spectrum upon which is superposed an emission spectrum from a highly excited gas which may form a nebulous shell around the star. Why some stars possess such shells while

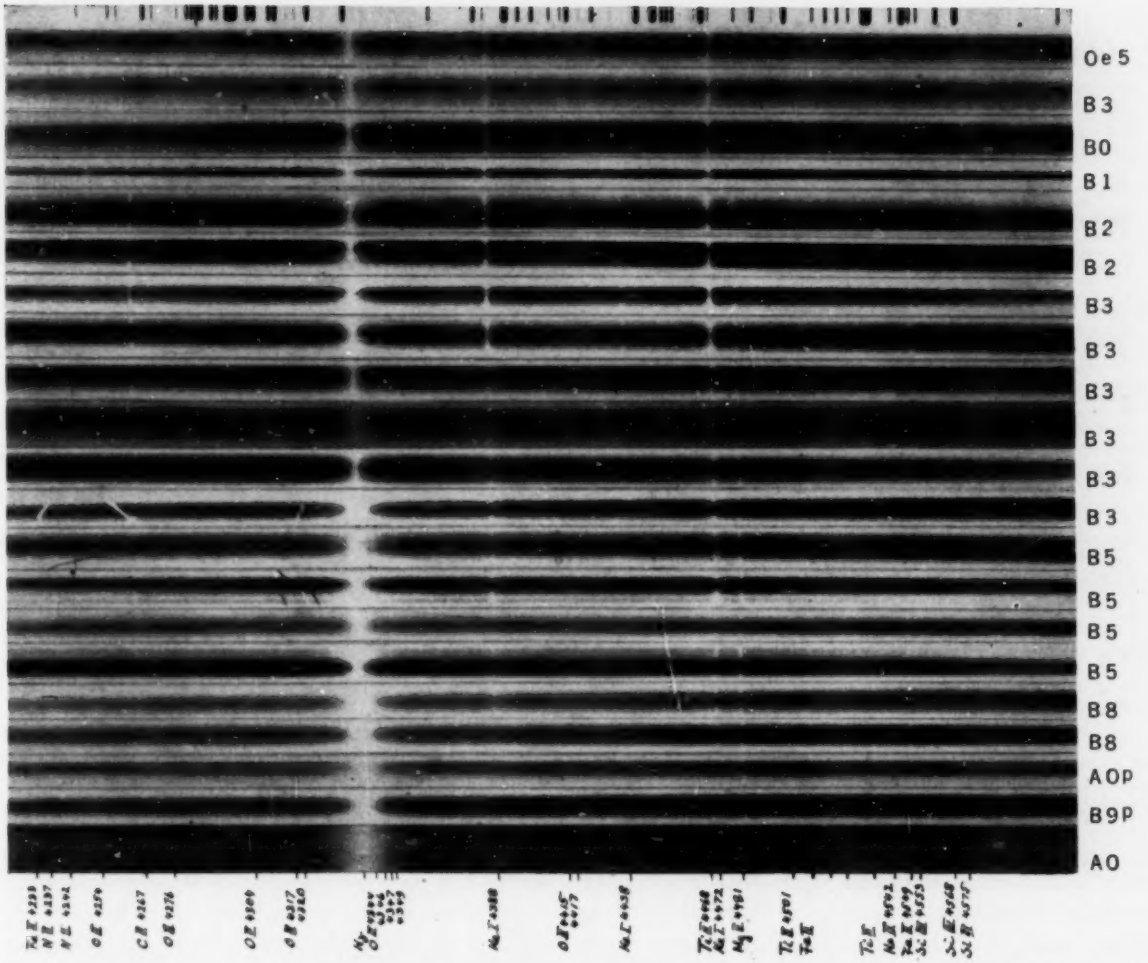

FIG. 2. A short portion of the sequence of stellar spectra, ranging in temperature from about 30,000°K at the top to 15,000°K at the bottom. The hydrogen line Hγ increases in strength as the temperature diminishes, as does also the line Mg II 4481. The lines of helium increase from the top to about spectral class *B2* or *B3*, and then gradually decrease, disappearing at *A0*. The lines of Fe II are invisible in the hotter stars and begin to appear at intermediate temperatures, increasing in strength toward the bottom. The great widths of the hydrogen lines show that the Stark effect is strong and that the pressure must, therefore, be large. Hence, these stars are small in size and are known as dwarfs.

others do not is not known. But we definitely know that the shells are not very stable structures, for the emission lines vary in intensity and structure. In some stars they periodically disappear and reappear. In others, where they are split in two symmetrical components, one component may become stronger while the other becomes weaker. Quite frequently the variation is not periodic.

The widths of the emission lines of any one element are proportional to the wave-length. Hence, we suppose that the broadening is caused by Doppler effect. In some stars, such as novae, Wolf-Rayet stars, and the P Cygni type stars, the shells expand, and this expansion may well account for the widths of the emission lines. We infer this from the fact that these emission lines are flanked on their violet sides by absorption lines—obviously produced in those parts of the expanding shells which are in front of the apparent stellar disks.

In many other stars, designated as Be stars, there are no violet absorption lines and we are therefore not certain whether the Doppler effect is caused by expansion or by some other type of motion. It could be due to turbulence or to axial rotation.

Some years ago a very significant correlation

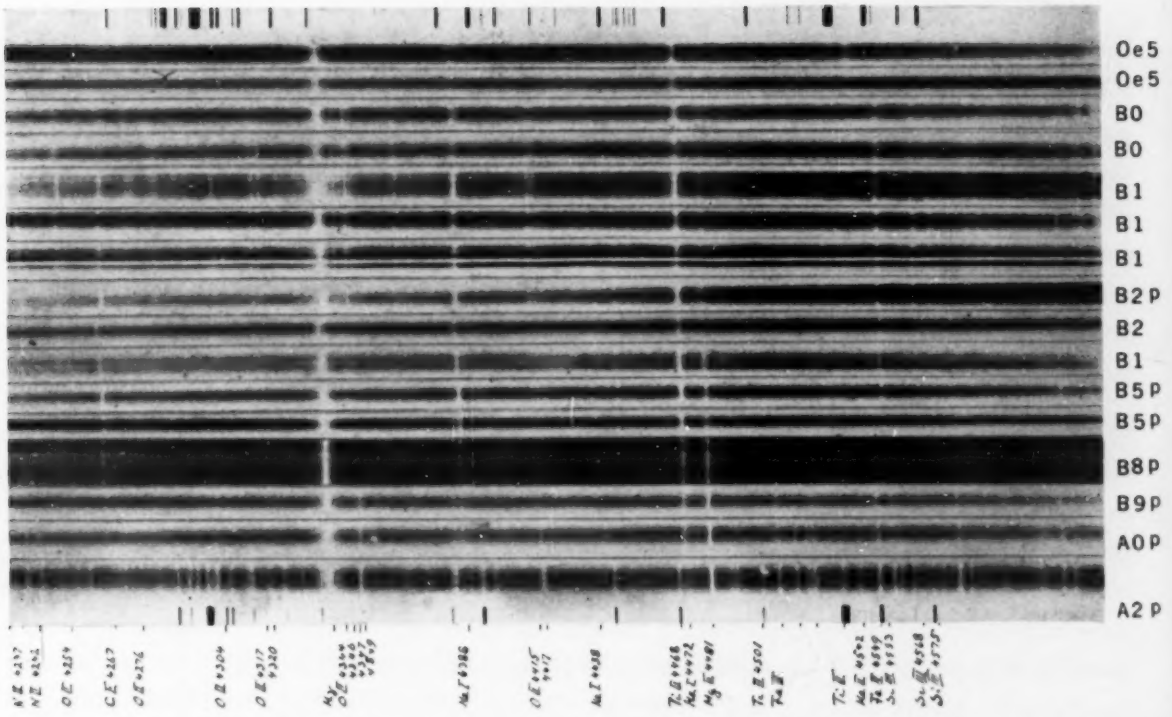

FIG. 3. A sequence of stars running parallel to that of the preceding plate and consisting of stars of high luminosity, or giants. All lines appear relatively strong and sharp but the hydrogen lines have no wings, showing that the Stark effect is weak. The great strength of the line Mg II 4481 is of particular interest in connection with the discussion concerning departures from thermodynamic equilibrium.

was discovered between the widths of the emission lines and the widths of those absorption lines—mostly of helium and ionized magnesium—which are not complicated by emission. The latter have contours typical of broadening produced by rapid axial rotation. Hence it is reasonable to suppose that axial rotation has something to do with the broadening of the emission lines.

But what is the nature of this correlation? Measurement of the widths of the emission lines shows that the corresponding velocity is not always the same as that found from the stellar absorption lines. For example, the absorption lines of π Aquarii give an equatorial velocity-component of rotation, in the line of sight, of 100 km/sec. The total width of the emission line Hβ is 7.5A. One-half of this would correspond to the rotational velocity. At Hβ a Doppler shift of 1A corresponds to 62 km/sec. Hence, the emission line would give a rotation of more than 200 km/sec. Similar discrepancies are found for other stars.

If the rotational velocities from the emission lines are always larger than those from the absorption lines, we might assume that the shells extend to great distances from the surfaces of the stars, so that if they should rotate as solid bodies the emission lines would be broader than the stellar absorption lines.

However, we find that the widths of the Fe II emission lines do not agree with those of hydrogen. Thus, in χ Ophiuchi we have:

Hβ	3A
Hγ	2.6A
Hδ	2.3A
Fe II	4.1A

We must conclude that either the Doppler effect is not one of rotation, or that the shell does not rotate as a solid body with the reversing layer of the star.

It is rather important that the cause of the Doppler effect be settled. Hence we inquire again into the possibility of turbulence or expansion. We have direct evidence in a few cases (φ Persei) that the tenuous gases of the

shell produce a deep and relatively narrow absorption line which appears as a central reversal in the middle of the emission line. These absorption lines are deep and completely devoid of Stark effect. Hence they cannot be due to the star's reversing layer; moreover, they cut deep into the emission and can hardly be produced in a lower layer than that which gives rise to the emission lines. The contour of the central absorption shows a small amount of turbulence, but not nearly enough to explain the widths of the emission lines. Is it possible that the absorption line is formed in a very high, quiescent layer while the emission lines come from a deeper, turbulent shell? It does not seem probable that this is the case. In general, the deeper layers which are closer to the photosphere produce the stronger absorption lines. In fact, the ratio of emission to absorption is sometimes used as a crude, yet fairly reliable, criterion of distance from the photosphere.

We are inclined to assume that the emission lines and the central absorption originate in the same mass of gas. If so, turbulence is ruled out by the narrow width of the central absorption, while expansion is ruled out by the fact that the absorption is central and not, as in the case of a nova or P Cygni star, on the violet edge of the emission.

It is significant that in φ Persei the central absorption is very much narrower than the normal stellar absorption lines. If the shell rotated with the star as a solid body the rotational broadening of the central absorption would be exactly the same as that of the stellar lines. The shell must rotate at a smaller angular velocity than the reversing layer, although it is quite probable that the linear velocity is much greater, accounting for the great widths of the emission lines. In φ Persei the order of magnitude of the rotational velocities from emission and stellar absorption lines is the same—about 200 km/sec. If the radius of the shell is ten times the radius of the star the rotational broadening of the central absorption will be reduced to 20 km/sec., which is quite compatible with the observations.

There is one serious complication: If rotation is responsible for the widths of the emission lines, it must vary with the distance from the star, and presumably decrease at very great distances. Hence it is, after all, not impossible that we observe a composite picture of many shells rotating with different angular velocities. We have as yet no means to study this effect in detail.

The next step in our study of the shell would be to measure the equivalent widths of the faint higher members of the Balmer central absorptions and to determine NH from formula (1). At present we can only estimate $N_2H=10^{14}$ for the number of hydrogen atoms in the second energy state per cm^2.

The emission lines can be used—but only with caution—for the determination of the total number of hydrogen atoms in the third level. The caution is necessary because there may be appreciable self-absorption. Since the energy distribution within the continuous spectrum of the star is known from its temperature and distance we can compare the energy emitted

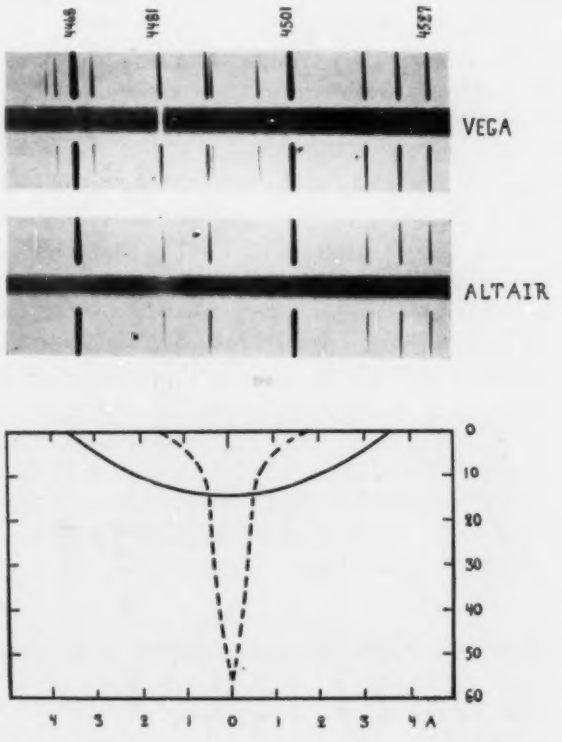

FIG. 4. Two spectra of the same class, corresponding to a temperature of approximately 12,000°. The measured contours of the line Mg II 4481 are shown at the bottom. The dish-shaped appearance of the line in Altair is due to the rapid axial rotation of the star.

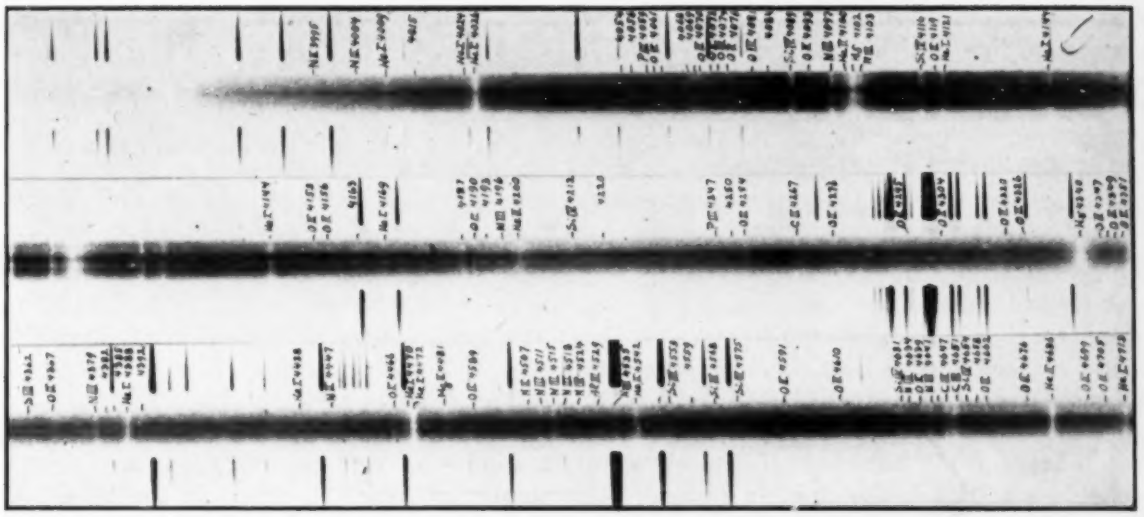

FIG. 5. The spectrum of the O-type star 10 Lacertae. The great widths of the He II lines 4200 and 4542 are caused by Stark effect.

within the entire emission line with that emitted within a width of 1A of the star's spectrum, and, finally, determine the number of atoms within the entire emitting shell.

The emission lines thus lead to a determination of $4\pi R^2 N_3 H$ while the central absorptions give $N_2 H$, where H is the thickness of the shell. A comparison of these two values should be instructive. If the ratio N_3/N_2 were known we could determine R. But, unfortunately, it would not be safe to assume that N_3/N_2 is given by Boltzmann's formula. The $2S$ level of hydrogen is metastable while the $3S$ level is not. Hence, we should expect that N_3/N_2 will in reality be much smaller than Boltzmann's formula predicts. The source of the exciting radiation is far from the gas and conditions depart markedly from those of thermodynamic equilibrium. It is only for equilibrium conditions that Boltzmann's formula holds. If the second hydrogen level were completely metastable we can express the number of atoms as

$$N_2 = N_1 e^{-(h\nu_{12}/kT)}, \tag{2}$$

while for the third level we have

$$N_3 = N_1 \beta e^{-(h\nu_{13}/kT)}. \tag{3}$$

We have disregarded here the statistical weights. β is the so-called dilution factor which measures the departure from thermodynamic equilibrium:

$$\beta = \tfrac{1}{4}(r/R)^2,$$

where r is the radius of the star and R the radius of the shell. Since $\nu_{12} \sim \nu_{13}$, for hydrogen, we may use

$$N_3/N_2 = \beta.$$

Since β is a function of R/r only, we could use our measurements of the emission and central absorption lines for the evaluation of R, provided we can estimate the value of r. In reality little is known regarding the lifetime of the $2S$ level of hydrogen. Computations by Breit[9] promise to throw light upon this important question.

It is possible that astrophysical observations will ultimately lead to an experimental determination of the lifetime of the $2s$ state. From corresponding lines in the Paschen and the Balmer series we can determine for the central absorptions $N_2 H$ and $N_3 H$. The latter quantity is what we want for our determination of R. The observed ratio N_3/N_2 will then give the departures from the pure Boltzmann factor.

These departures from thermodynamic equilibrium are of vital interest at the present time. Nearly all of our past work in stellar spectroscopy has been built upon the assumption that the populations of the various energy levels are determined by the Boltzmann formula. In

nebulae and interstellar space the departures are enormous. In the extended atmospheres, or shells, conditions differ less drastically from those of thermodynamic equilibrium, but the departures are by no means negligible.

Until about a year ago it was completely unexplained why the absorption spectra of shells frequently show Fe II, Ti II and many other elements, while the strong lines of Mg II and Si II are absent or very weak. In normal stars the latter are strong and conspicuous. It is not very likely that only these two elements should be subject to large variations in abundance. The question arose: What is common to Mg II and Si II, but is not shared by Fe II, Ti II, etc.? The answer is: The lower levels of the observed lines of Mg II and Si II combine by means of strong transitions with the ground levels of their respective ions, while the lower levels of all observable lines of Fe II, Ti II, etc. are metastable. This clue gave the correct answer to our puzzle. For a metastable level the Boltzmann relation (2) holds true even if the exciting source is at a great distance. But for a normal level the population is reduced in proportion to β. Hence, Mg II and Si II will be weakened, relative to Fe II, Si II, etc. in direct proportion to β, and we have here another valuable method for determining R/r.

When the dilution is large, atoms accumulate in the metastable levels and remain there long enough to permit occasional forbidden transitions. We then observe forbidden emission lines. In most stellar shells no forbidden lines are observed. Hence the dilution is not large enough or the pressure is not low enough to prevent removal by collisions or by radiation from the metastable levels. In some shells, however, forbidden lines of Fe II, Fe III, etc. are conspicuous.

The extraordinary weakness of Mg II and Si II in the absorption spectra of the shells is paralleled by an abnormal weakness of these lines in the emission spectra of many Be stars. These stars often have conspicuous lines of Fe II. It is, to say the least, surprising that Fe II is strong while Mg II is weak or absent.[10] The emission lines of Mg II 4481 were found as extremely weak and broad features in χ Ophiuchi and other Be stars. In χ Ophiuchi the width of bright Mg II 4481 is 5.7A, while Fe II is 4.1A and Hδ is 2.3A. If the broadening is caused by rotation, we should conclude that Mg II is produced at a lower level than Fe II or H. This suggests that strong dilution is unfavorable to the production of Mg II 4481—in agreement with our conclusions from the absorption lines of the shell. But it is not completely obvious why the emission line of Mg II should be weakened relative to the emission lines of Fe II. The upper levels of both sets of lines are normal, not metastable. Perhaps the fact that the upper levels of the Mg II and Si II lines cannot be reached from the ground level in one step, while the upper levels of Fe II, Ti II, etc. can be reached directly from the ground levels, has something to do with the problem. Thus, the computations by Wurm and Struve[11] show that for helium the normal level 2^3P which is not metastable, but which cannot be reached directly from the ground level

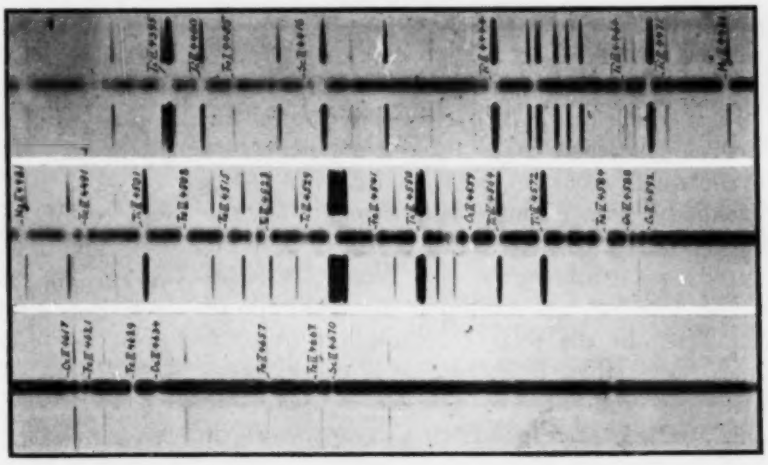

FIG. 6. The spectrum of ϵ Aurigae showing very strong lines of ionized iron, ionized titanium, etc. The contours of the lines are deep and have steep edges. They are very much wider than the instrumental contours due to the finite slit width, and their shapes are interpreted as being caused by turbulence in the atmosphere of the star.

1^1S is not nearly as much depleted by dilution as is the level 2^1P which does connect directly with the ground level. Hence it is quite reasonable to expect that Mg II and Si II will be weak in emission as well as in absorption. Only in exceptional cases, when the statistical equilibrium is seriously upset, can we expect recombination processes to produce strong emission lines of Mg II and Si II. But not even such abnormal conditions should produce strong absorption lines in the shell. Apparently Baldwin's[12] observation of strong emission lines of Mg II and Si II in the peculiar and rapidly varying spectrum of γ Cassiopeiae may be explained in this manner. It is significant that at no time in the development of γ Cassiopeiae did Mg II and Si II produce strong absorption lines in the shell.[13]

The variety of phenomena to be expected when the radiation is appreciably diluted is enormous. Bowen[14] has pointed out some special fluorescence phenomena in nebulae, and there is no reason why such abnormal excitations should not occur in the outer shells of stars. The variety of observed phenomena is only limited by the weakness of the spectral lines and by the scarcity of bright stars surrounded by shells. But Merrill's catalogue of Be and Ae stars[15] contains 416 objects most of which are within the reach of powerful spectrographs.

We have as yet no adequate theory to cope with the problems of departures from thermodynamic equilibrium. There is no doubt that such departures exist even in stellar atmospheres and it is to be hoped that the study of the shells may pave the way for a theory of stellar atmospheres in which these departures are accounted for.

There is another type of departure from equilibrium which has been particularly stressed by Menzel;[16] namely, that caused by a departure in the quality of the radiation from that of a blackbody. For example, the strength of the chromospheric emission lines of He II is interpreted as a consequence of a large ultraviolet excess. Unsöld[17] has computed that the ratio of He^{++}/He^{+} in the solar chromosphere is $10^{38.5}$ times larger than it should be if the extreme ultraviolet radiation of the sun, capable of ionizing He^{+}, corresponds to a temperature of 5040°K. Roughly, the intensity of radiation must be proportional to the excess.

The existence of a large ultraviolet excess may never be proved by direct observations. But the cumulative evidence from chromospheric phenomena, from considerations of the mechanism by which the corona of the sun is supported[18] and by terrestrial phenomena[19] is very impressive.

III. Advances in Observational Technique

The objective or mirror of a large telescope projects upon the slit of a spectrograph an image of the sky, the scale of which depends upon the focal length of the telescope. The slit admits a narrow strip of light from this image to the collimator and this light after being dispersed by the prism or grating is again brought to an image by means of the camera lens of the spectrograph. It is important to realize that the slit admits all light* from the original image in the focal plane, which corresponds to the width of the slit. If a star is surrounded by a nebulosity whose image is less than the width of the slit the spectrum of the nebulosity is recorded together with that of the star. Since the angular diameters of all stars, except the sun, are much smaller than the angular aperture of the slit, stellar spectra represent the composite effect from all parts of the star's apparent disk. Similarly, many double stars are recorded as composite spectra.

In the construction of an astronomical slit spectrograph special attention must be given to its efficiency in light. The principal considerations have been summarized by Keeler:[20]

A. 1. In all cases the collimator should have the same angular aperture as the telescope.

B. When the object observed is a luminous surface of considerable angular magnitude, such as the sun, moon or a large nebula:

2. The brightness of the spectrum is independent of the angular aperture of the telescope.

3. The brightness is independent of the linear aperture of the telescope.

4. The efficiency of the spectroscope as regards brightness is determined by its aperture, i.e., by the effective aperture of the collimator,

* We disregard here losses of diffraction produced by a very narrow slit.

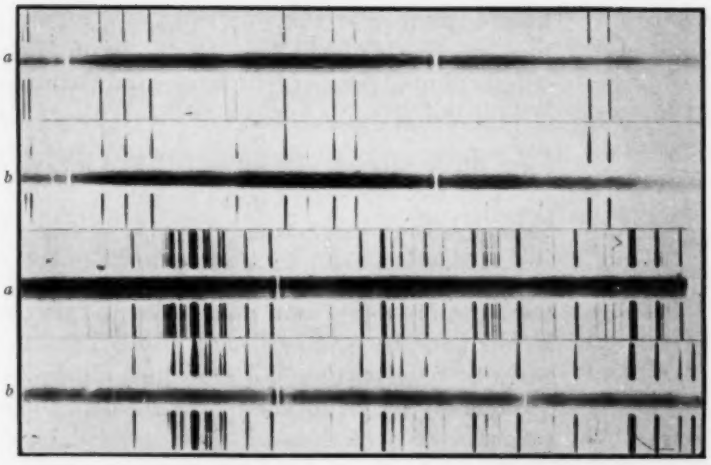

FIG. 7. The spectrum of φ Persei: (*a*) 1934, December 11; (*b*) 1935, January 24. The hydrogen lines consist of a sharp and deep central absorption flanked by two symmetrically placed emission lines which in turn are superposed over wide wings suggestive of Stark effect. The symmetrical arrangement of the lines suggests rotation rather than expansion as the cause of the widening of the emission lines.

the other parts of the instrument being of such dimensions as to transmit a beam of the same diameter.

C. When the object is of very large angular magnitude, as the sky illuminated by sunlight, the aurora, or the zodiacal light:

5. The spectra of objects whose angular magnitude is greater than the angular aperture of the telescope are best observed without a telescope.

6. The efficiency of a spectroscope for such objects, so far as brightness is concerned, depends upon the aperture of the spectroscope.

7. The same method may be extended to the sun and moon by using a sufficiently long collimator.

D. When the object is a star:

8. The brightness of a star spectrum is proportional to the area of the telescope objective, and independent of the aperture of the spectroscope.

9. The purity of the spectrum is proportional to the length of the collimator.

These simple considerations are sufficient for all practical applications. Since in reality star images formed by large telescopes are affected by "seeing" conditions of the atmosphere, they are intermediate between cases *B* and *D* of Keeler. Hence, to obtain an efficient stellar spectrograph it is necessary to use a telescope of large aperture and to make the collimator as long as possible. The focal length of the telescope is immaterial and the practical limit to the size of the collimator is set by the cost of the prisms and lenses required to accommodate the full beam.

The most important recent improvement in the construction of spectrographs is the invention of the "image-slicer" by Bowen,[21] a device which reduces the loss of light on the slit jaws of a stellar spectrograph. In a large telescope and under conditions of "bad seeing" the tremor disk of a star may have a diameter of as much as 10″. If the focal length of the telescope is approximately 20 meters (like the Yerkes 40-inch refractor), the linear diameter of the tremor disk is 1 mm. With a slit of 0.05 mm in width less than one-tenth of the light is utilized, the remaining nine-tenths being lost on the jaws of the slit. Only in nights of exceptionally "good seeing" is this loss reduced to less than a quarter of the available light.

The problem of saving the light lost at the slit jaws is especially important when a large stationary Coudé type spectrograph is used. The equivalent focal lengths of the two largest installations—at the 100-inch reflector on Mount Wilson and at the 82-inch reflector of the McDonald Observatory—are several times longer than that considered, so that the tremor disk may have a diameter of several millimeters. In these instruments, intended for work with high dispersion, the slit cannot be greatly widened, and the loss at the jaws may occasionally amount to almost 99 percent, or to a reduction in limiting brightness of almost 5 magnitudes.

The problem of "funnelling" the light lost on the jaws into the slit has been considered sporadically by many astronomers, but no satisfactory solution had been found until Bowen constructed the image-slicer. It is easy to see

that a pair of inclined mirrors arranged parallel to the slit will not solve the problem. Such a device would either increase the aperture of the beam at the collimator (where it would be lost) or would reflect the light back towards the sky.*

The principle of the "image-slicer" is extremely simple. We can consider the tremor disk of a star as the combined effect of a very large number of individual star images. Consider two such images: one centered on the slit, the other removed a small distance from it. There is no reason why we should not, by means of two 45°-reflections, shift the second image enough to make the light enter the slit. We cannot, however, superpose the two stars, because in that case one of the two plane mirrors would obstruct the light of the first star image. What we can do is to use very small mirrors, and, effectively, place the image of the second star image on the slit alongside that of the first image. Since by means of the two reflections we have increased the path only by an insignificant amount and since the displacement along the slit is also negligible, the second star image will after passing through the slit illuminate the collimator almost as well as the central image. We shall observe on the plate two spectra, corresponding to the two images. By means of a cylindrical lens placed a short distance in front of the photographic plate we can make the total width of the combined spectrum as narrow as we please.

The image slicer consists of a series of small mirrors arranged in such a way that a series of parallel "slices" of the tremor disk are laid *in tandem* along the slit. A cylindrical lens is used to reduce the width of the resulting broad spectrum.

In spite of the great practical difficulty of making the small plane mirrors, astrophysicists have justly claimed that the image slicer may be regarded as the greatest spectroscopic invention of modern times. H. N. Russell[22] recently remarked that "with the new device, the 100-inch telescope should accomplish as much as the 200-inch could do without it."

The performance of modern astronomical spectrographs has also been greatly improved in recent years. Large prisms can now be obtained which give practically perfect definition. The Coudé spectrograph of the McDonald Observatory employs two prisms made by Adam Hilger of light flint glass cast by Chance and Company in England. The dimensions of these prisms are:

First prism: Refracting angle 63° 30′; length of side 235 mm; thickness 120 mm.
Second prism: Refracting angle 31° 45′; length of side 205 mm; thickness 120 mm.

At the Mount Wilson Observatory important results have been secured with plane diffraction gratings ruled by R. W. Wood on aluminized disks of Pyrex glass. Dunham[23] finds that "the efficiency of second-order gratings ruled by R. W. Wood on aluminum films has been found to be almost equal in the blue to that of a train of prisms made from the most satisfactory glass obtainable. In the ultraviolet, green, red and infra-red, the gratings are definitely superior."

Another important improvement—developed by Adams and Dunham at Mount Wilson, and later extensively used at the McDonald Observatory—consists in the Schmidt camera as image-forming device of a stellar spectrograph. This camera consists of a spherical mirror, diaphragmed at the center of curvature and thus freed of coma. The spherical aberration is removed by a "correcting plate" placed in the center of curvature. The definition given by this instrument is excellent over a large field. Hendrix[24] at Mount Wilson has recently made two Schmidt cameras for stellar spectrographs each having a focal ratio of f: 0.66, and intended, respectively, for the Mount Wilson and the McDonald Observatories. Struve has successfully used Schmidt cameras of f: 1 and f: 2 in connection with the McDonald Observatory Cassegrain spectrograph, while Dunham[23] has used various types of off-axis parabolic reflecting collimators and of Schmidt cameras, rendering the system almost achromatic. The superb definition of these new instruments is shown by the discovery of many previously unknown absorption lines in regions of the spectrum previously investigated with spectrographs of older construction.[25]

Most American observatories have found it expedient to have the mirrors of their reflectors coated with aluminum. The process of evaporating the metal in a high vacuum, as developed by

* This remark is due to Professor Joel Stebbins.

John Strong[26] and R. C. Williams,[27] are very similar and the resulting properties of the aluminum coatings are also essentially similar.[28] The high reflectivity of aluminum in ultraviolet light has permitted astronomers to extend the range of their spectrograms as far as λ 3000 in the ultraviolet—this being close to the effective limit of transmission of the atmosphere. The importance of this extension has been very great. W. H. Wright[29] and his collaborators have greatly extended our knowledge of the physical processes giving rise to emission processes in planetary nebulae, by measuring and identifying many new ultraviolet emission lines. Boothroyd, Williams, Shaw and others[30] have made notable advances in the measurement of absorption lines. Even more important lists of lines have been secured by Adams and Dunham[31] and by Sanford[25] at Mount Wilson. More recently, Unsöld and Struve[32] have extended the lists of wave-lengths in the early-type spectra from plates secured with the Cassegrain quartz spectrograph of the McDonald Observatory. The most spectacular advance attributable directly to the use of aluminized mirrors is the discovery by Dunham and Adams[33] of interstellar lines of Ti II originating from the lowest sublevel of the ground term (^4F), which consists of four sublevels. While the lines arising from the lowest sublevel can easily be seen in the spectra of distant stars (λλ 3073, 3229, 3242, 3383), no trace was found of the lines originating from the next sublevel, having an excitation potential of only 0.012 volt. Dunham[33] states that in laboratory sources these lines are actually stronger than the ones which come from the lowest sublevel. Their absence in the absorption spectrum of the interstellar gas is accounted for by the fact that the radiation of the stars in interstellar space is extremely diluted, so that an atom after having reached (by recombination or by emission of a Ti II line) the $a^4F_{5/2}$ level has time to emit the forbidden infra-red line corresponding to the transition ($a^4F_{5/2}-a^4F_{7/2}$), although the lifetime of the upper state is believed to be of the order of 28 seconds.[34] Dunham points out[33] that "this astrophysical observation appears to be the only direct evidence for the existence of transitions of this type."

Important improvements have been secured in the past few years in the construction of spectrographs intended for large diffuse nebulae. Keeler's rule[35] C_5 had not previously been applied to these objects because their angular diameters are considerably smaller than the angular apertures of ordinary spectrograph collimators. Hence, Keeler had advised the elimination of the telescope only for very large sources, such as the aurora and the zodiacal light. Struve[36] has proposed a slit spectrograph for nebulae in which the telescope is eliminated, and the collimator is replaced by a slit about 25 mm in width and 63 cm in length, which is placed at a distance of 17.7 meters from the prism. There is no collimator lens, and the spectrograph camera—an f:1 Schmidt reflector—is focused at the slit. The sky is thus out of focus by a small amount, and a point is spread over an area of 16′ in diameter. In principle, this instrument is the fastest existing spectrograph for nebulae which have a uniform surface brightness over a circular area of at least 16′ in diameter. The instrument was attached to the Yerkes 40-inch refractor and has given excellent results.[37] Its gain in speed over the conventional type of spectrograph is due to the elimination of the telescope and the collimator lens.

A spectrograph based upon the same principle has been built at the McDonald Observatory.[38] A plane rectangular mirror serves as the slit and reflects the light of the nebula in the direction of the north pole. At a distance of 23 meters the beam is intercepted by a round plane mirror firmly mounted at right angles to the polar axis. This mirror returns the beam to the small equatorial mounting which supports the slit-mirror and the quartz prisms with the f:1 Schmidt camera. The effective distance from slit to prism is 46 meters and the spreading of the image is only 6′. Since two reflections from plane mirrors are used in this instrument it is appreciably slower than the one built for the Yerkes Observatory. Its advantages over a focal plane spectrograph attached to a large telescope are the absence of the collimator lens and the great angular length of the slit—about 1°.5 (2° at the Yerkes Observatory)—which permits the rapid exploration of large sections of the sky for very faint emission nebulosities many of which cannot be directly photographed.

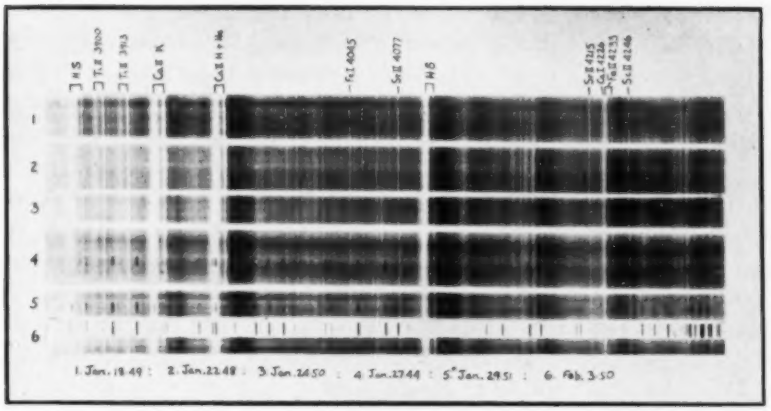

FIG. 8. The spectrum of Nova Herculis 1934, prepared for reproduction by Dr. Morgan and Miss Kellman. The emission lines of hydrogen and of other elements are flanked on their violet sides by double absorption lines, indicating that the shells are expanding with different velocities.

An exceedingly effective spectrograph equipped with a small telescope lens and a conventional short focus spectrograph has been used by V. M. Slipher[39] for the study of faint extended nebulosities in the Milky Way. The telescope lens forms a sharp image of the sky; hence the spectrograph integrates only over the width of the slit (which is fairly wide) and does not integrate over an additional area of the sky, as is the case in the Yerkes and McDonald instruments. It is readily seen that even with a small lens of a few inches in aperture and a moderate focal ratio the gain in resolving power in the sky is materially improved. Hence, for the investigation of small scale structure in nebulae, the focal plane spectrograph is preferable. But it requires a collimator of appropriate focal ratio. Both types of instruments have given valuable results—revealing, among other things, the existence of very large and extremely faint emission nebulosities in the Milky Way and in the outer portions of the constellation Orion. Since the background of the night sky produces its own characteristic emission spectrum superposed over a faint continuous spectrum, it is relatively easy to obtain the emission lines of the hydrogen Balmer series, the forbidden lines of ionized oxygen, etc. produced in the nebulae. The purpose of the nebular spectrographs at the present time is to reach the faintest possible surface brightnesses. The contrast between the nebular emission lines and the night sky background sets a limit to the emission intensities which we can reach. For hydrogen this lower limit corresponds to the emission of from one to ten atoms in the third energy level per column of 1 cm^2 in cross section. Such a column probably extends over a distance of several hundred parsecs, or approximately 10^{21} cm, being limited by the increasing amount of continuous absorption in cosmic dust clouds. We can thus detect a concentration of hydrogen corresponding to about 10^{-21} atom/cm^3 in the third energy level.

An entirely different problem is presented by the corona of the sun. This mysterious object had, until recently, been observed only during the brief minutes of total solar eclipses. One of the leading observers of solar eclipses, S. A. Mitchell, states that he has traveled about 90,000 miles to witness eight total eclipses and that the total accumulated time afforded him for observations has been approximately 15 minutes.[40] Less than one hour of observing has been available at all recent eclipses for the detailed spectroscopic study of the corona. Yet, the corona is by no means faint. It has about one-half as much light as the full moon and should thus be an easy object for high-dispersion spectrographs. But the uneclipsed sun is approximately 1,000,000 times brighter. It is the brilliant illumination of the atmosphere and the dust within it, and of the lenses and prisms of the instrument which has rendered futile earlier attempts by Huggins, Deslandres, Hale and many others to observe the emission lines of the corona without an eclipse.

It is one of the greatest triumphs of modern astrophysics that this problem has been successfully solved, in 1931, by B. Lyot[41] of the Paris Observatory. In a small observing station on the Pic du Midi in the Pyrenees, at an elevation of 2870 meters, Lyot found that the "sky near

the sun has a brilliancy of about one-millionth of the sun for λ 5500, which is not sufficient by itself to overpower the corona within a few minutes of the sun's limb."[42] But dust in the air must be avoided. At sea level, with a clear sky, it often surpasses 50 millionths of sunlight and is seldom less than 20 millionths. On the Pic du Midi, especially after a snowfall, the background of the sky is not more than twice as bright as the corona. To photograph the coronal spectrum Lyot had to eliminate scattering of light in the spectrograph. After a painstaking elimination of light diffracted by the edges of the lenses, light scattered by dust, scratches on the optical surfaces and small bubbles in the glass, Lyot obtained better results than any that had previously been secured during total solar eclipses.

One of the most fundamental works in stellar spectroscopy—the Henry Draper Catalogue of stellar spectra—has been completely based upon plates secured with objective prism telescopes. Since the stars are point sources they require no slit, if the telescope is accurately guided. In practice objective prism spectra have less resolution than slit spectrographs of comparable dimensions. The star images are often appreciably larger than the normal width of the slit; moreover, unsteadiness of the images due to rapid variations in the refraction of the air and errors in the guiding tend to make the narrow absorption lines relatively shallow. The principal advantage of the objective prism is the fact that it permits the photography in one exposure of the spectra of all stars, within a reasonable range of brightness, which fall within the field of the plate. The Draper Catalogue, completed in 1924, contains the spectra of 225,300 stars classified by Miss Annie J. Cannon at the Harvard Observatory. Extensions to fainter stars are being published from time to time at the Harvard Observatory.

The spectral types and the luminosities of the stars—also determined from spectroscopic criteria—form the most important information upon which we base our ideas of the structure of the galaxy. The Henry Draper Catalogue is complete only to about magnitude 8.5. For a luminous B-type star, having a temperature of 20,000°C and a luminosity 10,000 times that of the sun, this would correspond to a distance of about 5000 parsecs (one parsec equals 3.08×10^{18} cm) if there were no continuous absorption by dust in interstellar space. But we now know that there is a large amount of such absorption, so that the true distance of our typical star may be only 1000 parsecs. The diameter of our galactic system is of the order of 30,000 parsecs. Hence, we penetrate with our spectroscopic analysis to only one-fifteenth of the entire extent of the Milky Way. Slit spectrographs reach to much fainter magnitudes, but for statistical purposes it is necessary to accumulate a large amount of material, which is, of course, impossible if each spectrum must be exposed separately Hence there is a great demand for large instruments equipped with objective prisms. The Cape Observatory's 640-mm objective prism, used in conjunction with a refractor of 9 meters in focal length, is believed to be the largest now in existence.[43] The Harvard Observatory has a 600-mm objective prism for a parabolic reflector of the same aperture.

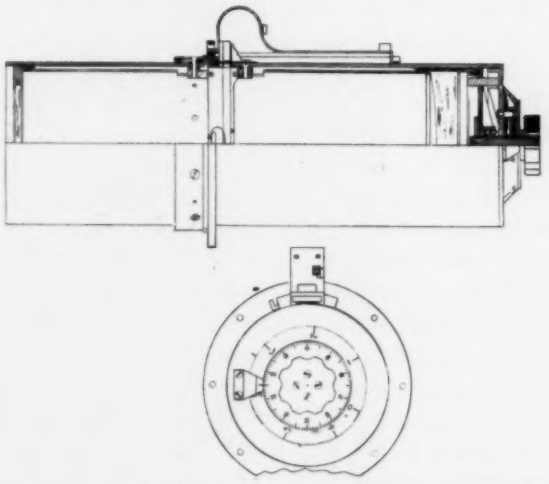

FIG. 9. The f : 2 Schmidt camera of the McDonald Observatory, used in connection with a quartz Cassegrain spectrograph. The images are formed by a spherical mirror diaphragmed at the center of curvature, and the spherical aberration is removed by a correcting plate in the plane of the diaphragm.

The advantages of the Schmidt telescope for objective prism work have been demonstrated by Schmidt[44] and others at the Hamburg Observatory in Bergedorf, Germany. A 40-inch (1 meter) Schmidt telescope with focal ratio f: 2, and equipped with an objective prism of

the same aperture is being planned for a new observatory near Rome, Italy.[45] It is probable that the extremely short focal ratio of this instrument will greatly reduce the limiting magnitude of the stars whose spectra could be photographed with it. The sky background is not spread out into a spectrum and thus retains its normal surface brightness, which should blacken a fast blue-sensitive plate in about 10 to 20 minutes. The stars, on the other hand, are spread into spectra and are therefore greatly weakened. With a dispersion sufficient for accurate classification as well as for the determination of spectroscopic luminosities, the limiting magnitude should be 14 or 15. On the other hand, it does not seem profitable to increase the focal ratio to more than about $f:2.5$, for otherwise the blurring produced by large star images would become quite troublesome.

The high cost of large objective prisms and the difficulty of mounting them in front of a large reflecting telescope has prevented their use in connection with the largest existing reflectors. However, a useful substitute is the so-called slitless spectrograph of which the most famous example is the quartz spectrograph at the Crossley reflector of the Lick Observatory.[46] A negative lens placed inside the focus of the large telescope mirror acts as the collimator and renders the beam parallel. After passing through the prism the beam is focused by a positive lens. A new slitless spectrograph for the McDonald Observatory is the outcome of discussions by several members of the Yerkes Observatory staff and has been designed by E. L. McCarthy.[47] The prism, placed a short distance from the focus of the 82-inch mirror, has an elliptical spot covered with aluminum which reflects the beam at an appropriate angle. A parabolic mirror of 248 mm in aperture and 608 mm in focal length serves as the collimator. The parallel beam is then dispersed by the 32° prism and is focused by a Schmidt camera having an equivalent focal length of 304 mm. The unvignetted field of the spectrograph is about 0°.5. The effective focal ratio of the reflector is reduced from $f:4$ to $f:2$. This is advantageous because it reduces the tremor disk of the star. McCarthy has investigated the optical properties of the new instrument and has found that the parabolic collimator removes the coma and the astigmatism of the large mirror. Actual spectrograms secured by Greenstein and Seyfert in June, 1939, show that all expectations have been fulfilled.

In this connection attention may be called to the new slitless spectrograph of the Greenwich Observatory.[48] This instrument was intended for the determination of the distribution of energy in the continuous spectra of individual stars, and therefore did not require a large field. But a slit spectrograph is not suitable for this type of work because atmospheric dispersion spreads the light of a star into a spectrum the length of which varies with the zenith distance. Hence, a narrow slit may not be equally illuminated by light of different wave-lengths and serious systematic errors vitiate the results. Hence, a slitless spectrograph must be used. The Greenwich observers, Greaves, Davidson and Martin[48] placed a convex Cassegrain mirror in such a position that its focus coincides with the focus of the telescope mirror. The parallel beam thus obtained enters a prism at the lower end of the telescope and is focused by a parabolic reflector.

One of the principal difficulties in spectrophotometric work on the spectral energy distributions of stars is the great range in photographic densities which must be measured. To obtain the best results the entire range must lie within the straight-line portion of the photographic characteristic curve. Intensity ratios greater than 1 : 100 (or 5 stellar magnitudes) are not readily measurable in one step, and in practice much smaller ratios are to be preferred. In a stellar spectrograph the transmission of the optical system gradually decreases on the violet side and at the same time the linear dispersion increases, while the sensitivity of the emulsion drops rather abruptly on the red side. Hence, the density of a stellar spectrogram usually decreases from about $H\gamma$ toward the violet and unless one wishes to restrict the work to a narrow range in wave-lengths it is often necessary—especially in the cooler stars—to measure large differences in photographic density. An ingenuous method to reduce this difficulty has been proposed by Couder[49] and applied by Chalonge and Vassy[50] and later by Arnulf, Barbier, Chalonge and Canavaggia[51] to stellar spectra. In this procedure advantage is taken of the astigmatism of a lens

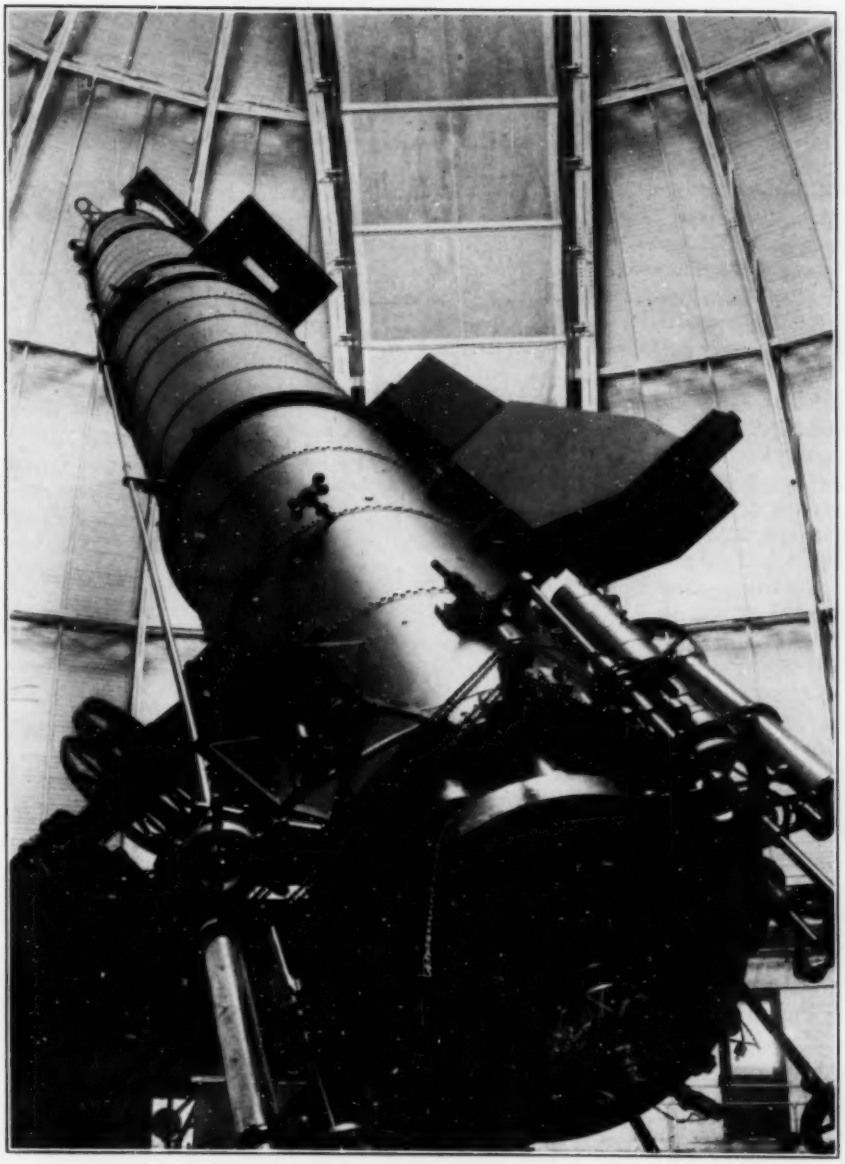

FIG. 10. Nebular spectrograph attached to the Yerkes 40-inch refractor. The slit is at the upper end of the tube and the diaphragm is placed halfway between the tube and the prism, in order to cut out the light from the night sky. There is no image-forming telescope lens and no collimator lens. The $f:2$ Schmidt camera with two quartz prisms mounted in front of it is focused at the slit, 58 feet away.

inclined to the beam. The lens is turned by a small angle—about 8°—around an axis parallel to the refracting edge of the prism. The astigmatism of the lens then draws out the star image into a line of uniform brightness, perpendicular to the length of the spectrum. Since the amount of this widening depends upon the inclination of the beam to the optical axis it is different for different wave-lengths. Chalonge and his collaborators incline the lens in such a way that the weak ultraviolet part of the spectrum is widened least (0.7 mm at λ3100) while in the brighter blue part of the spectrum the widening is greater (1.3 mm at λ4861).

Bibliography

1. Clerke, *History of Astronomy* (1902), p. 133.
2. Adel and Lampland, Astrophys. J. **88**, 182 (1938).
3. Saha, Bull. Harvard Obs., No. 905 (1937), p. 1.
4. See, for example, Davis, Astrophys. J. **86**, 109 (1937); Bobrovnikoff, Astrophys. J. **89**, 301 (1939).
5. Swings and Edlén, Astrophys. J. **88**, 618 (1938).
6. Öpik, Astrophys. J. **81**, 177 (1935); **86**, 203 (1937).
7. Struve, Astrophys. J. **78**, 81 (1933); Morgan, Astrophys. J. **77**, 330 (1933); Morgan, Pub. Yerkes Obs. VII, Part III (1935), pp. 10–11.
8. Unsöld, *Physik der Sternatmosphären* (Springer, Berlin, 1938).
9. Breit, unpublished.
10. Struve and Swings, Astrophys. J. **75**, 161 (1932).
11. Wurm and Struve, Astrophys. J. **88**, 98 (1938).
12. Baldwin, Astrophys. J. **89**, Plate XVII (1939).
13. Baldwin, Astrophys. J. **89**, 269 (1939).
14. Bowen, Astrophys. J. **81**, 1 (1935).
15. Merrill, Astrophys. J. **78**, 87 (1933).
16. See, for example, Astronomical Symposium, Hudson, Ohio, 1938, p. 99.
17. Reference 8, p. 420.
18. Reference 8, p. 453.
19. Reference 8, p. 425.
20. Keeler, Sidereal Messenger **10**, 442 (1891).
21. Bowen, Astrophys. J. **88**, 113 (1938).
22. H. N. Russell, Scientific American, January, 1939, p. 15.
23. Th. Dunham, Jr., Pub. A.S.P. **50**, 220 (1938).
24. Hendrix, Pub. A.S.P. **51**, 158 (1939).
25. See, for example, R. F. Sanford, Pub. A.S.P. **50**, 244 (1938).
26. John Strong, Astrophys. J. **83**, 401 (1936).
27. R. C. Williams, Astrophys. J. **77**, 316 (1933); Phys. Rev. **41**, 255 (1932).
28. Williams, Astrophys. J. **89**, 611 (1939).
29. W. H. Wright, Pub. A.S.P. **46**, 32 (1934).
30. Boothroyd *et al.*, Astrophys. J. **80**, 1 (1934); **80**, 7 (1934); **82**, 87 (1935); **83**, 225 (1936).
31. Adams and Dunham, Astrophys. J. **87**, 102 (1938).
32. Unsöld and Struve, unpublished.
33. Dunham and Adams, Proc. Am. Phil. Soc. **81**, 279 (1939).
34. Dunham, Nature **139**, 246 (1937).
35. This paper, p. 809, C, 5.
36. Struve, Astrophys. J. **86**, 613 (1937).
37. Greenstein and Henyey, Astrophys. J. **86**, 620 (1937).
38. Struve, Van Biesbroeck and Elvey, Astrophys. J. **87**, 559 (1938).
39. V. M. Slipher, Pub. Am. Astr. Soc. **9**, 168 (1939); **9**, 229 (1939).
40. S. A. Mitchell, *Eclipses of the Sun* (Columbia University Press, 1932), p. xvii.
41. Lyot has summarized his results in Zeits. f. Astrophys. **5**, 73 (1932), and The Observatory **62**, 145 (1939). Excellent illustrations are given by him in L'Astronomie **51**, 203 (1937); **52**, 193 (1938).
42. Dyson and Woolley, *Eclipses of the Sun* (Oxford, 1937), p. 108.
43. W. Schaub, *Handbuch d. Experimentalphysik*, **26**, 267 (1937).
44. Schmidt, *Jahresbericht der Hamburger Sternwarte in Bergedorf für das Jahr 1931.*
45. H. von Klüber, Die Sterne **19**, 125 (1939).
46. W. H. Wright, Lick Obs. Bull. **9**, 52 (1917). (A small instrument based on the same principle has been in use at the Lick Observatory since 1902. Lick Obs. Bull. **2**, 46 (1903).)
47. E. L. McCarthy, unpublished.
48. Greaves, Davidson and Martin, *Observations of Colour Temperatures of Stars* (1932), p. 11. See also, The Observatory **57**, 160 (1934).
49. Couder, Comptes rendus **197**, 1199 (1933).
50. Chalonge and Vassy, Rev. d'optique **13**, 113 (1934).
51. Arnulf, Barbier, Chalonge and Canavaggia, J. des Observateurs **19**, 149 (1936).

Here and There

Cover Photograph

The cover photograph shows a recent spectrographic installation of the Department of Industrial Hygiene of the School of Medicine, University of Pittsburgh. The equipment shown has been adapted especially for the investigation and diagnosis of occupational health hazards and industrial poisoning. An enclosed arc and spark source, an optical bench and a large quartz prism spectrograph are shown.

Calendar of Meetings

November	
13–17	American Petroleum Institute, Stevens Hotel, Chicago, Illinois.
15–17	American Institute of Chemical Engineers, Providence, R. I.
December	
1–2	American Physical Society, Chicago, Ill.
4–9	17th Exposition of Chemical Industries, Grand Central Palace, New York, New York.
27–30	American Association of Physics Teachers, Columbus, Ohio.
27–Jan. 2	American Association for the Advancement of Science, Columbus, Ohio.
28–29	Sixth Chemical Engineering Symposium, Ann Arbor, Mich.
28–30	American Physical Society, Columbus, Ohio.
28–30	Geological Society of America, Minneapolis, Minn.
January	
22–26	American Institute of Electrical Engineers, New York, N. Y.
February	
22–24	American Physical Society, New York, N. Y.
22–24	Optical Society of America, New York, N. Y.

New Appointments and Promotions

Dr. Fritz London, formerly of the Institute Henri Poincaré, one of the divisions of the University of Paris, has been appointed Professor of Chemistry at Duke University, Durham, North Carolina. Dr. London is a theoretical physicist, whose work has dealt with problems related to chemistry. Among his contributions in this field are his development of a theory of the origin of van der Waals forces and, with Heitler, of a theory of valence. In recent years he has been interested in the properties of matter at very low temperatures, such as superconductivity, and also the relation of atomic and molecular structures to the magnetic phenomena.

★

Dr. Gerald F. Tape, formerly Graduate Assistant in Physics at the University of Michigan, has been appointed Instructor in Physics at Cornell University for the current year.

Cornell University

During the academic year 1938–39 and summer of 1939 reports by nonresident speakers were presented at meetings of the faculty and graduate students in physics at Cornell University as follows:

Sept. 26 **"Photo-conductivity and the Theory of the Latent Image."** N. F. MOTT, *University of Bristol.*

Oct. 20 **"The Philosophical Interpretations and Misinterpretations of the Quantum Theory."** PHILIPP FRANK, *German University of Prague.*

Nov. 7 **"Some Metallurgical Problems from a Physicist's Point of View."** S. DUSHMAN, *General Electric Research Laboratory.*

Dec. 1 **"The Separation of Isotopes by Chemical Methods."** H. C. UREY, *Columbia University.*

Jan. 16 **"Behavior of Matter under High Pressure."** EDWARD TELLER, *George Washington University.*

Mar. 6 **"Design and Construction of the Large Westinghouse Electrostatic Generator."** W. E. SHOUPP, *Westinghouse Laboratories.*

Mar. 20 **"Cloud Chamber Studies of Cosmic Rays."** J. C. STREET, *Harvard University.*

Mar. 27 **"Proton Reactions."** L. A. DUBRIDGE, *University of Rochester.*

May 1 **"High Pressure Research."** P. W. BRIDGMAN, *Harvard University.*

May 15 **"The Self Energy of the Electron."** V. F. WEISSKOPF, *University of Rochester.*

July 31 **"Problems of the Pick-up Tube in Television."** E. G. RAMBERG, *Research Division, Radio Corporation of America.*

Aug. 7 **"Some Significant Developments in Nuclear Physics."** S. W. BARNES, *University of Rochester.*

New Books

Second Report on Viscosity and Plasticity—prepared by the Committee for the Study of Viscosity of the Academy of Sciences at Amsterdam. Second edition. Pp. 273+viii, Figs. 98, 18¼×26¼ cm. Nordemann Publishing Company, New York, 1939. Price $7.00.

This is a continuation of a series of articles on viscosity, plasticity, and the structure of matter, which has been published by the Committee for the study of these phenomena of the Academy of Sciences at Amsterdam starting with the "First Report" in 1935. The second report contains investigations concerning the structure of liquids (J. M. Burgers), on the viscosity of liquids in connection with their chemical and physical constitution (F. M.

Jaeger), on the motion of small particles of elongated form, suspended in a viscous liquid (J. M. Burgers), on the yield value (R. Houwink), on recent plastometers (C. J. van Nieuwenburg) and on technical capillary viscometers (R. N. J. Saal).

One of the authors states that the whole subject of the internal structure of liquids is in a state of intense development and that this collection of papers was considerably influenced by the general discussion on the structure of liquids held and published by the Faraday Society in 1936.[1]

Ever since the success of the kinetic gas theory, it was the aim of investigators to develop a theory of the viscosity of simple liquids. The first and second chapters of the book are devoted to this subject, to cohesion and viscosity of liquids, the object being to describe the mechanism by means of which the interatomic exchange of momenta operates when the atoms are densely packed as in the liquid state, and to predict in an analogous manner to the kinetic theory of gases the viscosity of simple liquids from atomic data. Several of these new theories of the liquid state are reviewed and equations discussed in which stress and strain rate are related or viscosity and temperature or viscosity and specific volume. The shape of the molecules is considered (whether spherical, elongated or disk-like, etc.). In connection with the problem of lubrication the structure of thin liquid layers is discussed (W. B. Hardy's experiments). A long chapter is devoted to special applications of the flow of a viscous liquid around solid spheres or elongated bodies. This leads to a mathematical discussion of the viscosity of suspensions in liquids, in which the work by G. B. Jeffery was outstanding. Formulae are given for the apparent viscosity of a shearing motion in a liquid layer containing small solid particles of an elongated shape in a suspension. Under the heading, "The Yield Value" first relations between stress, strain and rate of strain are discussed for various kinds of substances. Several definitions are introduced for mechanical properties which will probably not appeal much to the group of men acquainted with the technical flow of the ductile metals. It has been stated elsewhere at a similar occasion that engineers have good reasons for declining to accept some of these definitions or terms, which have made their appearance in a few recent publications mostly devoted to a discussion of the plastic properties of very soft or amorphous substances. For example, "the value of the shearing stress which brings about the first indication of a permanent deformation" is called, "the lower yield value." Since the phenomenon of the upper and lower yield points of mild steel is known (about thirty years), engineers have followed C. Bach (who first described the peak of the stress-strain curve in mild steel) by calling the stress at which first yielding of *steel* starts the "upper yield stress." The stresses required for deforming a ductile metal are called "hardening yield values" ("yield stress," "*Fliesspannung*" are accepted expressions). Other unusual combinations of terms could be quoted from this article.

It seems to the writer that this renaming of names and defining of certain known properties could have been avoided by relying on the terminology already in existence, which was developed in connection with the testing of the most widely used engineering materials of construction (steel, ductile metals, etc.).

Since it must be admitted, that many important properties of the new plastics and of many soft and amorphous materials are very similar from a mechanical point of view to the corresponding properties of the metals at low and at elevated temperatures—which latter have been investigated by engineers and described much earlier in connection with the plastic flow and the creep of the ductile metals—it would seem natural that these earlier experiences now available should influence the terminology for the flow of soft substances and also the trend of the ideas. However, this latter does not seem to have been much the case.

As already stated, much space in these articles has been given to considerations of the atomic mechanisms of flow in crystalline and amorphous substances. The last two chapters contain the description of methods and of instruments measuring viscosity. There seems to be no principal difference between those termed "plastometers" and the ones called "viscometers." Under the former ones, instruments helping to measure the function connecting stress and rate of strain are understood—for more viscous substances, while the latter ones serve more for fluid substances. Although reading of these abstracted papers is by no means easy, this collection of papers will be welcomed by those who wish to obtain information about the theories of flow of soft substances.

A. NADAI
Westinghouse Electric & Manufacturing Company

[1] Trans. Faraday Soc. **33**, 1–282 (1937).

Proceedings of the Sixth Summer Conference on Spectroscopy and Its Applications. GEORGE R. HARRISON. Pp. 172+vii, 19×25 cm. John Wiley and Sons, Inc., New York, 1939. Price $2.00.

This book, according to its editor, Dr. George R. Harrison, should be considered a "compilation of discussions of a rapidly developing field from various aspects." As such, it is a very useful and timely publication both for the industrial-spectrochemical analyst and for the more academic worker in this field. A few of the topics presented in the 31 papers will show this. They are: spectrochemical analyses of minerals, plants, vitamins, enzymes, patent medicines, gases and dyes; the usefulness of the spectrograph in criminal investigations; new developments in instruments, light sources, spectroscopic plates, quantitative techniques and theories of latent-image formation; and, finally, descriptions of the very important publications, "Standard Wavelengths," "Bibliography of Spectrochemical Analysis, 1920–37," and "New Tables of the 100,000 Principal Spectrum Lines of the Chemical Elements between 10,000A and 2000A."

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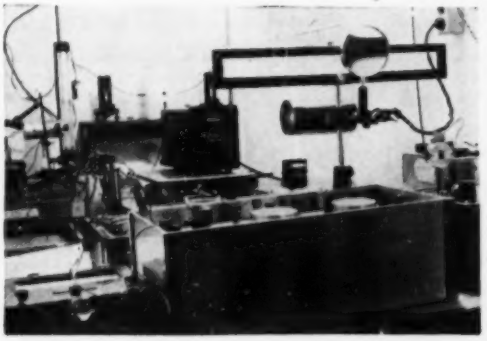

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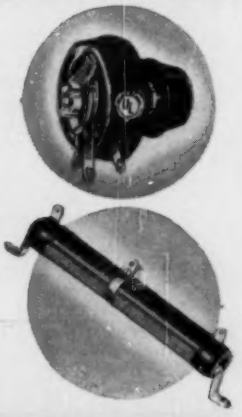

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